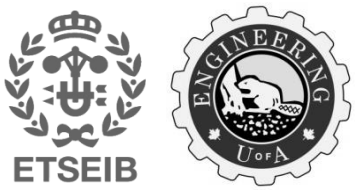

Characterization of Time-Dependent Properties of Thick Composite Section in Fiber Reinforced Polymers Flywheel Rotors

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Abstract

This project is focused in the research of a suitable model to characterize the time dependent mechanical properties of fiber reinforced polymers as the viscoelastic behavior. This model will be based in experimental data obtained from several tests that have to be designed and performed, in this thesis several procedures are designed and tried with up to 4 different testing machines and procedures which involves dynamic mechanical analyzer, and different models of electromagnetically based testing machines from BOSE company, using either water bath chambers and convection oven chambers for temperature control.

The final purpose is to predict long term creep compliance and stress relaxation in a FRP flywheel rotor that has to be built and assembly in the future, this will guarantee safety and the integrity of the rotor after assembly and during its lifetime. More than fifty compression tests have been conducted using cubical specimens cut directly from the winding rotor and tested in the transverse direction which was the critical dimension. The material tested was a composite made of epoxy (EPON 826 with the curing agent Epikure 9551) reinforced with glass fiber in the circumferential direction of the flywheel rotor.

The results of the tests show that the initially proposed variables for describing the viscoelasticity such as the temperature, the age of the polymer and the stress level of load applied have no confirmed correlation with the creep response, and hence further research is needed.

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1 Preface

1.1 Project Origin

This research is part of a bigger project entitled “Rotor Design for High-Speed Flywheel Energy Storage Systems”. A flywheel storage system consists of a fast spinning rotor that is speed up or slowed down via an electrical motor or generator. When excess energy is available, for example, from renewable energy systems such as wind or solar-power, electrical energy is converted by the motor into kinetic energy which is thus stored in the rotating mass of the flywheel, i.e. the rotor. When electrical energy is needed, this process can be reversed by using the generator functionality. The chosen fiber-reinforced polymer composite is beneficial for the rotor due to its long-term performance and specific material strength that are superior compared to metallic materials. The rotational speeds of the rotor are substantial reaching 10^4 revolutions per minute. Resulting stresses are correspondingly high. Therefore, an in-depth knowledge of the material behavior is needed to ensure safety over a long time of operation.

1.2 Motivation

The present work has been constantly motivated by the global energetic problem. Improvements in energetic efficiency are struggling, however further efforts in this field are needed to minimize the impact that humans have on the environment. Recently innovative energy storage systems have been investigated in order to increase the efficiency performance of all kind of machines, electrically powered or not. It is great to be part of a multidisciplinary and innovative project that attempts to solve issues about efficiency, and more specifically, in the case of this thesis, the safety of the Flywheel Storage System.

Personally, I have some experience in designing and prototyping but I have never had the opportunity to work in the experimental field, so the six months duration of this project is a great chance to acquire skills and understand how it feels to be experimenter.

2 Introduction

2.1 Objectives

This project aims to characterize the mechanical time-dependent properties of the flywheel material which is developed at the Mechanical Engineering department of the University of Alberta. As such, the final objective is very extensive but it is not specific. Below is a list of the specific goals to reach by the end of the thesis:

1. Explain and summarize in a simple way the primary known theories about the mechanical response of polymers and composites.
2. Secure enough parameters to characterize the creeping response and the stress relaxation response of the material at the most critical working condition of the flywheel.
3. Validate experimentally the theoretical models chosen.
4. Complete all the experimental tasks in a maximum period of 5 months.
5. Guarantee the short and long term safety of the flywheel
6. Provide guidelines to improve the flywheel's rotor to a safer one.
7. Provide useful information for the next student in order to continue the research done in this thesis.

2.2 Scope

This project will focus on developing and executing suitable experimental procedures in order to explain the behavior of the materials involved into creating the rotor. As the rotor is made up of three rings, each one with its own material, the ideal case will be to perform similar experiments for each material in order to fully understand the behavior of the entire rotor. But as the time is limited to five months and the only ring created until now is the internal one (Fiber + Epon826-Epikure 9551 matrix), the main effort is going to characterize the internal ring. As such, the thesis is not limited to the understanding of this material.

Furthermore, this project will base its predictions in well known ideas, principles, and theories. This suggests that no further formulations or new principles are searched. There will be a discussion of the results obtained experimentally, the suitability of the model chosen, and also an estimation of the maximum error made.

Finally, this project will include a computer model to predict the response of the ring at critical working conditions.

3 Viscoelasticity

In this chapter there are basic albeit useful ideas about viscosity in order to fully understand the choices made in this project. The general knowledge about viscoelasticity is explained including mathematical models, main theories and suppositions and microstructure's behavior that causes changes in properties in time.

To provide a basic definition of what is a viscoelastic material, essentially it is the material that combines both elastic and viscous behavior at the same time i.e. it has an instant response and a time-dependant response. This is caused by a molecular rearrangement. When a stress is applied parts of the long polymer chain change positions, this movement is called creep. While this is occurring it creates a back stress in the material which tends to stop the creep and at some point the back stress equals the applied tension and then the material no longer creeps. In addition, if the original stress is taken away, the back stress will cause the polymer to return to its original form so the material recovers. If the recovery is total, the material is called anelastic i.e. anelastic materials represent a subset of viscoelastic materials with a unique equilibrium configuration that allows them to fully recover after removal of a transient load. Another important feature of viscoelastic materials is that they suffer a hysteresis in the stress-strain curve and consequently, energy is lost while this process is carried out.

3.1 Viscoelastic Models

Time dependant properties involve models which obviously have time as a variable. There are many mathematical models that try to give the answer to the strain response of the material given its load history and its properties. Such models usually express the time dependency of the response in terms of an integral or differential definition. In this subchapter, the most known representations are described such as the "integral model" based on the Boltzmann superposition theory and the "differential model"; the information have been extracted from [1] but those models are widely known in polymers field and many publications make reference to them, so they are validated through a wide range of materials, most of them polymers. The goal of this thesis is to discover whether they also succeed in explaining the response of the studied material that is actually a composite. This fact may be relevant as composites are made of two different components and the creep response of these components may differ from typical polymers response. However this does not mean that is the first composite studied at long term response [2] is an example of similar studies done before, but in fact is less common.

3.1.1 The Integral Model

The integral model is a common way to call the model that derives from the Boltzmann superposition theory. It may be stated as follows: The creep in a specimen is a function of the entire loading history. Each increment of load makes an independent and additive contribution to the total deformation. If a specimen is loaded and is creeping under load, then the addition of an extra load will produce exactly the same additional creep as if that total load had been applied to the unloaded specimen and it allowed creeping for the same amount of time.

To exemplify the Boltzmann theory it is interesting to see ***Figure 3—1*** where it represents the response of two different steps blue and green solid lines starting and finishing at different

times and the response of the load as the sum of those steps which actually satisfies the expression (Eq.1).

$$\varepsilon\big(\sigma_1(t)\big) + \varepsilon\big(\sigma_2(t)\big) = \varepsilon(\sigma_1(t) + \sigma_2(t)) \qquad \text{(Eq.1)}$$

In the literature we have found statements saying that Boltzmann superposition does not imply linear scaling [3]. But it is relatively simple to realize that linear scaling is just a specific case of the Boltzmann theory where you add two or more loads at the same time. As such, from (Eq.1) it is trivial to arrive to (Eq.2) it is as simple to consider that σ_1 is proportional to σ_2 and it is applied exactly at the same time.

$$\varepsilon\big(c \cdot \sigma(t)\big) = c \cdot \varepsilon(\sigma(t)) \qquad \text{(Eq.2)}$$

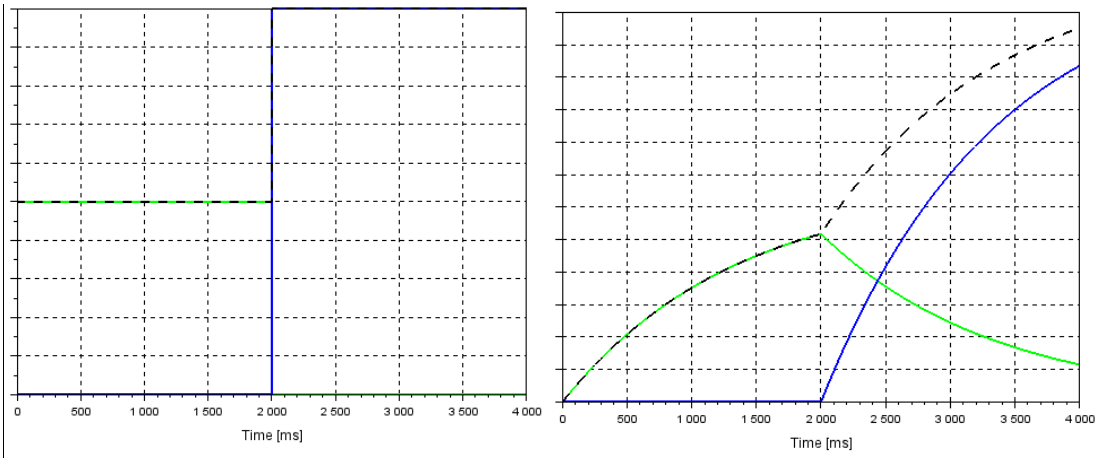

Figure 3—1. *Load steps applied (Left). Strain response (Right).*

The Boltzmann model has many implications due to the fact that it declares that the load history as relevant and additive. Hence the strain response is calculable from any load sequence knowing some constants or properties of the material simplifying this way the characterization of the material.

3.1.2 The differential model

Similar to the Integral model, the differential model allows for prediction of the response of the strain given the load history, but in this case, it is based on differential equations. Furthermore this model uses combinations of springs and dashpots in series and/or in parallel to define the differential equations so it is based in a Hookean-Newtonian system. Springs, which theoretically deforms instantly, are Hookean and the dashpots, which deforms continuously over time, are Newtonian. In the differential model there are many sub-models each with its own considerations and implications namely Maxwell, Kelvin-Voigt, Zener, N-Parameters are the most important but not the only ones.

Maxwell model is very simple; it only uses a spring and a dashpot in series therefore it implies that the stress is equal in each element but the strain is the sum of the strains. Using these two elements, we get the differential equation to a stress relaxation test (Eq.3), which integrated results in the exponential law (Eq.4).

$$\frac{d\sigma}{\sigma} = -\frac{E_m}{\eta_m}dt \qquad \text{(Eq.3)}$$

$$\sigma = \sigma_0 \cdot \exp\left(-\frac{E_m}{\eta_m}\right) = \sigma_0 \cdot \exp\left(-\frac{t}{\tau}\right) \; ; \; \tau = \frac{\eta_m}{E_m} \qquad \text{(Eq.4)}$$

The Kelvin-Voigt model also uses the same two elements to represent the strain response but in this case the elements are placed in parallel. Hence, while the strain is equal in each element, the stress is the sum of the stresses. The response of a creep test using this model is shown at (Eq.5).

$$\varepsilon = \varepsilon_0 \cdot \exp\left(-\frac{t}{\tau}\right) \qquad \text{(Eq.5)}$$

Both Kelvin-Voigt and Maxwell are the simplest models created to explain viscoelasticity in terms of springs and dashpots but they are vitally different. While Maxwell cannot explain the response to a creep test but it fits perfectly in a stress relaxation test; Kelvin-Voigt is exactly the opposite. The first model that actually can explain both behaviors must contain at least three components, two dashpots and one spring or two springs and one dashpot. This model is known as Zener model or also called Standard Linear Model, it is very useful because it can predict creep and stress relaxation but on the other hand it is more complicated. The basic equation of Zener model is shown in (Eq.6).

$$\frac{d\varepsilon(t)}{dt} = \frac{\frac{E_2}{\eta} \cdot \left(\frac{\eta}{E_2} \cdot \frac{d\sigma(t)}{dt} + \sigma(t) - E_1\varepsilon(t)\right)}{E_1 + E_2} \qquad \text{(Eq.6)}$$

Despite the fact that the standard linear model is very practical it is necessary to use more parameters to characterize the response of some materials. The called N-parameters model can be useful as you can build your own configuration using any amount of dashpots and spring. As it is logical, the more elements you have, the more accurate the model fits the data, but in most cases after 4-5 elements, the accuracy's raising is negligible.

3.1.3 Quasi-linear model

Although the previous models can be applied in the most situations, there are materials that cannot be described just by using linear viscoelasticity such as biological tissues like ligaments and collagen. While in linear viscoelasticity the compliance function and the stress relaxation function do only depend on time and thus the shape does not change by applying different stress or strains levels. In non-linear model the shape does change. Furthermore the relaxation function is separated into a function of time and a function of strain. So we have shape $E_t(t)$ of the relaxation function that is equivalent to the linear relaxation function and a second factor "g(ε)" that scales the shape depending on the strain applied. In this way, the real relaxation function is the multiplication of those two factors as it is shown in Eq.7. Realize that if g(ε)=ε then it becomes the already explained linear model. Hence Boltzmann superposition can be applied [4].

$$E(t,\varepsilon) = E_t(t) \cdot g(\varepsilon) \qquad \text{(Eq.7)}$$

To characterize the quasi-linear model, it is necessary to do the same experiments from the previous models. This way, you get the shape of $E_T(t)$ function as it is actually the called master curve in which you can extract information for prediction. However, in this case it is not enough. You also need to perform several experiments to determine the function g(ε). Combining these two functions you will have your quasi-linear stress relaxation function. Additionally, the function g(ε) is not completely arbitrary, it usually follows the rule that a study about non-linear ligaments [5] show, this is that the rate of stress relaxation decreases with increasing strain and the rate of creep decreases with increasing stress. This means that the more force you apply the more solid-like it becomes exactly as the aging effect explained in subchapter 3.4. Hence both, aging and non-linearity seems to perform in our favor as the more solid-like the material becomes the better performance the press-fit is going to have. Therefore, if we can demonstrate these two behaviors, we can guarantee that when extrapolating data to greater stresses and further ages the error committed is actually making it safer even if you don't consider those effects.

3.2 Microstructure

Aside from understanding the mathematical behavior of the material, the physical phenomena that causes these behaviors are interesting to understand and can be helpful at further stages of the project and/or for further studies as microscopy analysis.

As it was explained previously, it is possible to get any amount of models by using Maxwell and Kelvin-Voigt elements. However, the springs and dashpots involved can be physically explained by just 4 molecular interactions [6]. Each of these correspond to a different element in a four-element model as is shown in ***Figure 3—2***.

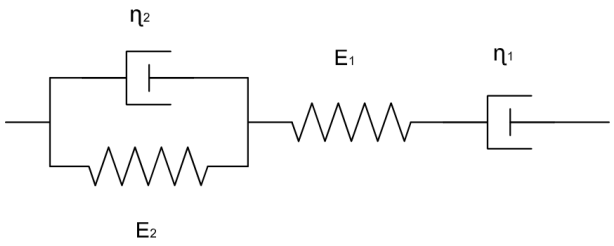

Figure 3—2. *Four-element model representation.*

The first interaction corresponds to the Maxwell spring (E_1) and is due to the tendency of the inter-atomic bonding to achieve equilibrium angles. Hence the response is instantaneous. This type of elasticity is thermodynamically known as "energy elasticity." In ***Figure 3—3*** it is a representation of this inter-atomic angles as part of the chain. At the top of the figure there is a relaxed chain, while at the bottom there is a force applied in the same chain so the inter-atomic bonds trying to restore the equilibrium shape. The second interaction is brought about by friction between molecules when slipping one from the other. As this force doesn't have any contribution to the material's recovery, it represents the Maxwell dashpot (η_1). The third interaction (Kelvin-Voigt spring E_2) is called "entropy elasticity." It represents the restoring force caused by thermal agitation of the chain segments, which tends to return oriented chains

to their most random configuration i.e. the highest entropy configuration. And the fourth interaction is the Kelvin-Voigt dashpot η_2. This can be explained by the resistance of the polymer chains with coiling and uncoiling caused by entanglements. As this behavior requires the motion of many chain segments, the process cannot occur instantaneously. Both the third and fourth interactions are represented in ***Figure 3—4***. It is shown two chains interacting through the entanglements, resisting the separating force (third) and also the tendency to the chains to get disordered.

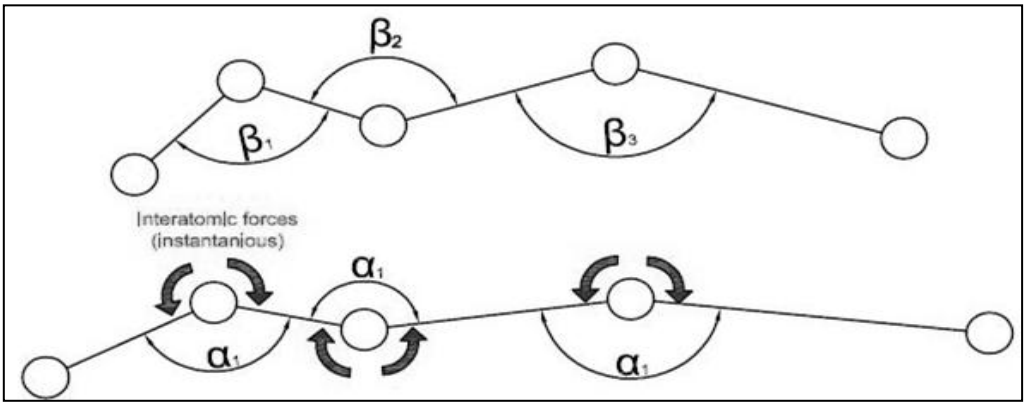

Figure 3—3. *First interaction.*

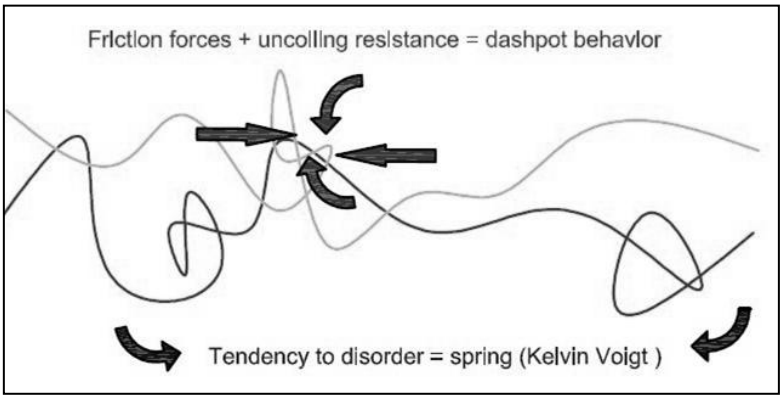

Figure 3—4. *Third and fourth interaction.*

These explanations about the microstructure help a great deal in the understanding of the models shown in the previous chapter as all of them are based on the dashpots and springs mentioned in the differential method. However, there are other theories that are important to comprehend about polymers and composites that might have an important role on the current project such as the Time Temperature Superposition Principle, which will be the base of the experimental procedures designed in this thesis.

3.3 Time Temperature Superposition Principle

There is a well-known principle about viscoelastic materials such as polymers and composites that provide good experimental tools to characterize viscoelastic properties. This principle is called the “Time Temperature Superposition Principle” or for short, TTSP. The reason it is so important and practical at experimenting and getting time dependant results is the fact that it can reduce the experimental time by a great factor, hundreds of times or even more. This principle basically correlates the time and the temperature as two completely interchangeable properties that interact with the material in a very similar way i.e. the idea behind is that if you

want to know the properties of a material after 1 year of load you do not need to run a test for 1 year to get the results but instead you can run an equivalent test at high temperature for a short period of time and you will get the same material response.

The capability of this principle appears to be very useful but care must be taken because not all the viscoelastic materials behave under this principle. Only the so called thermo-rheologically simple materials do [7]. These materials can be defined as "materials that by changing the temperature, the complete compliance spectrum is affected by the same degree". The general expression must follow Eq.8, where "D" represents the compliance of the material and b_T and a_T are shift factors, vertical and horizontal respectively.

$$D(\lambda, T_1) = b_T \cdot D(a_T \cdot \lambda; T_2) \quad \text{(Eq.8)}$$

$$\log(a_T) = \frac{C_1 \cdot (T - T_r)}{C_2 + (T - T_r)} \quad \text{(Eq.9)}$$

$$\log(a_T) = \frac{U}{2.3 \cdot R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right) \quad \text{(Eq.10)}$$

It is important to note that Equations 8, 9, 10 and TTSP itself are just empirical relationships, but they agree well with data for a wide variety of polymers. The shift factors used to shift the data horizontally (scaling time) and vertically (scaling compliance) should fit Eq.9 or Eq.10. The first was found by Williams-Landel-Ferry and it is called WLF equation. It fits well when the data is obtained over T_G. To get the variables you must choose one of your curves as a reference for which temperature is going to be the reference temperature T_r. Exactly the same equation applies to b_T. Any abrupt change in the shift factors indicates a sudden change in physical or chemical properties like thermal degradation, phase changes and so on. This equation represents the behavior of the material above T_G very well, you may even chose the universal constants C_1=17.44 and C_2=51.6 as an approximation, but under T_G this expression does not fit the data very well as many experiments have shown[8]. Additionally, the WLF equation has an asymptote at $C_2+T=T_r$, and shape changes completely thus the Temperature chosen is relevant. However T_r is normally the temperature with more data because it can be chosen as the master curve from which you will shift it to any other curve.

On the other hand, the Arrhenius equation corresponds to Eq.9 and it fits better the data under T_G. This equation uses the variables: U which is the activation energy, R which is the universal gas constant T which is the absolute temperature, and T_0 which is a constant. In this case, in order to fit the data the only parameter you have to know is the activation energy of the material U.

In this thesis we will perform experiments to see whether these empirical relations are correct for the specific composite used in the flywheel, but in the first place we must assume that our material is thermo-rheologically simple unless the data contradicts this. This is helpful due to the fact that the time to perform the experiments is restricted to six months.

3.4 Aging

With TTSP we have found that with few experiments we can get the shift factors minimizing the least squares of error of the difference between the data and the equations 7, 8 and 9 but the momentary master curve made with this data does not include the effect of aging. Therefore in order to achieve a complete characterization you need to consider the possibility of the material aging. This usually means the composite increases stiffness in time. Although the stiffer it becomes, the better performance it will provide for the flywheel press fit we do not want to neglect this effect in the first place. Furthermore TTSP alone cannot predict long-term creep. According to [3] even the shape of the curves is going to be different. In fact, TTSP can only predict long-term creep near the glass transition where the aging effect can be neglected.

3.5 Measuring Methods

From the integral and differential model we have seen that the strain response is related to the load history and vice versa. This suggests that the two simplest and intuitive ways to measure viscoelasticity are the creep test and the stress relaxation test. However there are other ways that involve the frequency domain that can be fast and give some clues about the behavior of the material.

Time domain tests such as creep and stress relaxation are relatively easy to perform using general compression or tensile test machines that allow obtaining information during the time the test is running. The only difficulty of using the time domain test is a considerable amount of time is needed to observe the response. Although the TTSP can help to reduce the time of the test, using this principle, there is the extra capability of the machines in order to control the temperature precisely which is not trivial and it may induce other errors such as thermal dilatation or sensitivity of the load cell or the strain gauges.

On the other hand the frequency domain based methods are much quicker compared to time domain methods but they need are complex machines that are capable of at least applying sinusoidal loads and/or strains. Consequently these tests take advantage of the fact that for a load history which is sinusoidal in time, the deformation history is also sinusoidal in time with a phase shift provided the material is linearly viscoelastic and the apparatus is linear [9]. Then, the phase angle between the load and the deformation is essentially equal to the phase angle "δ" between stress and strain. Basically this phase shift represents the viscous effect of the response as it is the retardation time for the strain to follow the load.

The measure of "δ" can be performed in different ways. The simplest way is by determining the time delay between the sinusoids using an oscilloscope [9]. Another common way is by using a graph of load versus deformation which is sinusoidal in time. This graph is called "Lissajous x-y figure" [9] and the shape shows is elliptic, provided that the material is linear, in this case δ can be obtained from Eq.11, where A is the horizontal thickness of the ellipse and B is the full width of the figure.

$$\sin(\delta) = \mathrm{A}/\mathrm{B} \qquad (\mathrm{Eq.11})$$

In order to get the information of the sinusoidal response many devices can be used. For example: the pendulum device, resonant ultrasound spectroscopy, piezoelectric ultrasonic

oscillator, a rheometer or DMA. To have a better insight of the basics of these devices, piezoelectric ultrasonic oscillator, rheometer and DMA are explained below. The first method is based on a device that consists of two piezoelectric crystals and a specimen cemented together. One crystal is driven electrically to induce vibration; the oscillating voltage induced by the strain in the other crystal is measured. The viscoelastic properties of the specimen are inferred from electrical measurements upon the sensor crystal and from the dimensions and masses of the specimen and crystals [9]. In a rheometer, the sample is subjected to sinusoidal rotational deformations and the resulting torque is measured. Since the sample's dimensions are known, the shear stress and the shear strain can easily be determined. The complex shear modulus is then calculated from the stress amplitude, the strain amplitude, and the phase angle. Similarly, DMA measures and generates the strain and stress sinusoids (For example in a single cantilever position), and from them the complex modulus E^* can be easily determined by knowing the maximum amplitude of the stress applied "σ_A" and the maximum amplitude of the strain response "ε_A" (see Eq.12). Then, the complex modulus can be obtained by using Eq.13 and Eq.14, in which, E' and E'' are respectively the storage modulus and the loss modulus.

$$|E^*| = \frac{\sigma_A}{\varepsilon_A} \qquad \text{(Eq.12)}$$

$$E'(w) = |E^*| \cdot \cos(\delta) \qquad \text{(Eq.13)}$$

$$E''(w) = |E^*| \cdot \sin(\delta) \qquad \text{(Eq.14)}$$

All of these methods are useful to understand the vibrating characteristics of the material as the energy dissipated during each cycle can be known. They can also be useful to determine if the viscoelasticity is linear or if there is a specific range where it is. Furthermore it can give insight about the aging effect explained in subchapter 3.4. However, in order to determine the long term creep under constant stress, in no sinusoidal and no-cyclical forces it is more adequate to perform a time domain rather than frequency domain experiment considering that there is a more direct relation with the elements in the differential model (dashpots and springs) and the constants we get from those experiments complete the equations needed to create a finite element model that is capable of predicting the behavior over a wide range of situations.

4 Material Modeling

In the previous chapter we have described the main theories and the general knowledge about viscoelasticity which we are going to use to design the experiments. In chapter 4 we will compress the information from chapter 3 to provide the designing of one single equation capable of predicting the response of the material.

The mathematical model proposed is also based on further simplifications taken from [3]. It states that the characterization will be complete using a simplification of a 4 parameter model by using the Taylor series to discard the high order derivative elements of creeping response i.e. the equation remain as Eq.15. Additionally, we will consider the material as linear in the first place and also that the material follows Time-Age superposition and Time-Temperature Superposition Principle. Considering these simplifications and using equations 8 and 10, we get the full strain response of the material concentrated in Eq.16 that takes into account a total of 6 parameters; three of them represent the exponential law extracted from Taylor series simplified from the 4 elements model, and the other three parameters characterize temperature and aging response.

$$D(\lambda) \approx D_0 + D_1 \cdot \lambda^m \qquad \text{(Eq.15)}$$

$$D(\lambda, T_1) = b_T \cdot \left[D_0 + D_1 \cdot \left(1 - e^{-a_t \cdot \frac{\lambda(t)}{\tau}}\right)\right] \qquad \text{(Eq.16)}$$

The parameters needed for modeling the reference curve give the shape of the reference curve i.e. a exponential law where D_0 is the elastic compliance that represents the instant response, D_1 is related to the creep compliance and represents the time dependant response. And finally τ is the time constant that is associated to the retardation of the response.

The shift factors needed for the temperature response are a_T and b_T defined in our case by using the Arrhenius formulation as the working temperature of the flywheel under the glass transition temperature. Therefore, a_T depends on the activation energy constant of the material U_1 and b_T depends on the activation energy U_2 as it is shown in Eq.17 and Eq.18

$$a_T = 10^{\frac{U_1}{2.3 \cdot R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \qquad \text{(Eq.17)}$$

$$b_T = 10^{\frac{U_2}{2.3 \cdot R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \qquad \text{(Eq.18)}$$

For characterizing the aging response only one parameter is needed μ_e depending on its value Eq.19 or Eq.20 are used respectively.

$$\lambda(t) = t_e \cdot \ln\left(1 + \frac{t}{t_e}\right) \text{ if } \mu_e = 1 \qquad \text{(Eq.19)}$$

$$\lambda(t) = \frac{t_e}{1 - \mu_e} \cdot \left[\left(1 + \frac{t}{t_e}\right)^{1-\mu_e} - 1\right] \text{ if } \mu_e < 1 \qquad \text{(Eq.20)}$$

Once all of these parameters have been determined, using for example the least squares minimization of the data obtained, the model is completed. Then it is possible to calculate the strain history for any stress history considering that Boltzmann superposition and linearity have been checked, similar procedure had been taken in [2]. In order to calculate the strain history for a constant stress the result creep response is easily determined from Eq.16 but the response for any random stress story has to be determined with a more complex formulation such as the *Volterra Integral*, also called *Boltzman superposition Integral* which basic expression is shown in Eq.21 Although this is the most precise way to calculate the strain response, it can also be calculated discretizing the arbitrary and continuous load history into small steps and superposing the creep responses.

$$\varepsilon(t) = D_0 \cdot \sigma + \int_0^t \Delta D(t-\tau) \cdot \frac{d\sigma}{d\tau} d\tau \qquad \text{(Eq.21)}$$

It is especially useful if the stress is represented as values from a list that we call σFUN(t) and the reference momentary strain curve ε(σ,t) at a certain age and temperature is known, and also discretized in a list that we are going to call REF(*t*), where REF(*n*) is the value placed in position *n* and it represents the time. Considering this, the strain value at times t=1, t=2, t=3 … (expressed in milliseconds or even smaller units) are placed at positions n=1, n=2, n=3 … of our list REF(t). Then the response can be calculated from a single summation shown in Eq.21. Hence this equation is the general expression used to evaluate the strain at any time in a simple way using programs like Matlab® or Scilab®. This expression is only valid if the starting point of the stress history is zero i.e. σFUN(1)=0.

$$\varepsilon(n) = \frac{\sum_{i=1}^{n} REF(n+1-i) \cdot (\sigma FUN(i+1) - \sigma FUN(i))}{\sigma_{ref}} \qquad \text{(Eq.22)}$$

This self made equation Eq.22 is a quick method to find the strain response for any stress function. But if *n* is high (for example $n=10^8$) then it starts to lose efficiency because, as the effect of the first stress step is already steady and does not change its value the firsts terms of the summation can be substituted by a constant. Thus there are less added terms and hence it reduces the computer time required in order to get the solution.

5 Experimental Data Acquisition

5.1 Introduction

In order to get all the material constants previously presented in chapter 4 it is necessary to obtain a robust amount of information from data that agrees well with viscoelastic theory, to do so good experimental setup must be designed.

The approach needed to get the results has been influenced by [2] in which it is explained the successful experimental setup and Specimen configuration for a carbon fiber reinforced thermoplastic polyamide. However studies [10] and [11] have also helped to design the experiments which have been analyzing long term behavior of respectively poly (ether ether ketone) and polyurethane foam. In this thesis the studied material is a composite made of Hexion Epon 826 (Epoxy) reinforced with glass fibers. The known characteristics we had previous to the experiments made are shown in the ***Table 5-1*** and they are provided by the supplier.

Property	Value
Tensile Modulus E_1 [GPa]	38.6
Transverse Modulus E_2, E_3 [GPa]	8.27
Shear Modulus G_{12} [GPa]	4.14
Shear Modulus G_{23} [GPa]	2.80
Poison ratio η	0.26
Density [kg/m^3]	1300
Thermal expansion coefficient α_L[1/K]	54 e-6

Table 5-1. *Properties of Glass Fiber reinforced epoxy Composite.*

Notice that these properties are estimations as they depend on the fiber density which could be different at any point of the flywheel's rotor. Additionally they do not include the compression properties for the E_1, E_2 and E_3 which in the particular case of E_1 is very different from the tensile value. However a first approximation off the compressive response can be the value of the Transverse Modulus as the fibers do not play a relevant role restraining the forces. Furthermore the epoxy (without reinforcement) has an E modulus of 5 GPa which is the same in any direction as it is an homogeneous or isotropic material. All of these properties have been used to run numerical models in previous research but there is a lack of information about this material, which this thesis tries to cover, that is the creep.

As previously mentioned, the main safety issue we want to guarantee is that the stress in the rotor made by the press fit is not decreasing to critical values after the relaxation of the material, which again we have no knowledge about. Thus, all the effort in the characterization will be around the long term response, specifically the compressive response (although this work is not restricted to it), that is the most relevant in terms of safety considering that the stresses generated by the press fit of the three rims of the flywheel are mainly compressive.

5.2 Experimental procedures

As it is said in the introduction of this chapter, the experiments performed in [3] (which are really similar to experiments performed in [2]) have influenced the decisions made in this project. Both projects are based in TTSP and Time-Age Superposition. However, the materials

that we are managing are different and the accessibility to testing machines is also different. As such the methods in this thesis vary slightly from the literature revised. A total of 4 different testing machines have been used for getting data and several different procedures to obtain the final specimens have been carried out.

5.2.1 Glass Transition Temperature

When polymers reach a certain temperature, its properties begin to change quickly within a range of temperatures, after that, the properties stabilize. The glass transition temperature (T_G) characterizes this range of temperatures, and it is usually defined as the middle temperature of the interval. The very first thing we have to know before designing the TTSP test is the Glass transition temperature (T_G) of our material in order to choose a suitable range of temperatures for the tests, all of them of course below T_G, if not, the Arrhenius Equation Eq.16 cannot be used.

Additionally T_G has effects on the age of the polymers, there are two types of viscoelastic materials depending on whether the response of these materials varies with time (aging material) or not (unaging material). Usually the more loads they have and the older they are, the more solid-like they become. Most of the polymers (or all of them) are aging under glass temperature, but when they work near the glass transition zone, the aging becomes negligible as it has been said in subchapter 3.4. Finally polymers are capable of being rejuvenated by keeping their temperature above T_G during at least 30 min.

Generally, in the case of Epoxies, T_G is strongly dependant on the cure schedule and other parameters like moisture affect it as well. However they have a T_G between 60°C to 170°C. As a prediction we have estimated the value of ours at the middle of that range 115°C. But obviously an experiment has to determine the real value. There is several ways to measure this. Differential Scanning Calorimetry (DSC) is a common way to measure it, as the heat flow has a peak or an off-peak in the glass transition if the transition is endothermic or exothermic respectively. Another usual method which is called dilatometry is based on the dilatation of material. Finally DMA can show the T_G as a peak in the phase angle or a rapid decay in the storage modulus. We have chosen the DMA method because of its accuracy and because we had rapid access to a Dynamic Mechanical Analyzer on campus localized at *Lipid chemistry group* lab.

The Dynamic Mechanical Analyzer used in this research is the model *DMA2980*. This instrument can control the force up to 18 N with an accuracy of 0.0001 N and it measures strain up to 10000 µm with an accuracy of 0.5 µm. The frequency range goes from 0 to 200 Hz with an accuracy of 0.01 Hz. During an experiment, the raw signals measured are force and amplitude and the driven force is constantly readjusted to match the test design.

The configuration of the experiment is *single cantilever*; this position is recommended for sub T_G tests, which is our case. Furthermore, in the *single cantilever* test, the sample should have a relation between length and thickness greater or equal to ten. As such, in order to change the stiffness of the specimen you can increase or decrease the thickness but always respecting 1-10 (thickness-length) relation. In the ***Figure 5—1*** the view of the DMA is shown as well as the clamps used to perform the T_G tests. The middle clamp is attached to the mobile shaft and the fixed clamps are the right and/or the left.

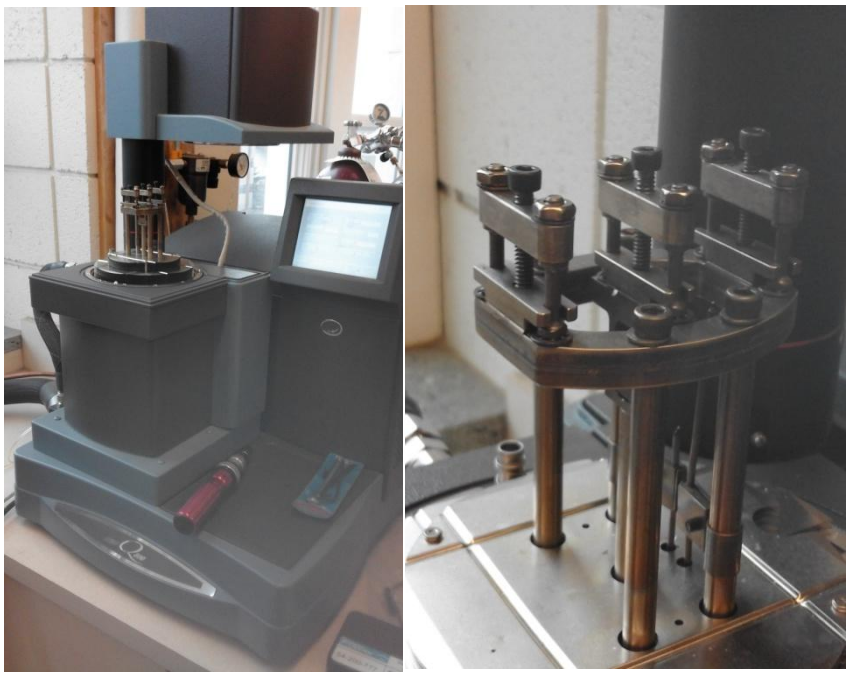

Figure 5—1. *DMA (Left). Clamps configuration suitable for single and dual cantilever (Right).*

In order to have the possible error made in the test and the reliability of it, two specimens have been tested. The specimens were rectangular rods with 48x12x3.4 mm dimensions each, both the original and the replica. The procedure was exactly the same for both and it is explained as followed. The specimens were fixed with the clamps shown in ***Figure 5—1*** and a sinusoidal force of 1 Hz frequency was applied on the mobile clamp with an amplitude of 9 N while the temperature was increasing from -40°C to 200°C using the standard convection oven of the DMA. Considering that the prediction for T_G was 115°C the initial recommended temperature for the sweep is under room temperature so liquid Nitrogen was needed to cool down the air of the oven below zero degrees.

Figure 5—2 displays the results of both responses, the first and second specimen, blue and black lines respectively, as it is evident they are very close one from one another and the peak of the *tan(δ)* happens to almost be at the same temperature. The value of T_G has been chosen as the maximum of the *tan(δ)* phase. Although other parameters could be chosen and there is no consensus in scientific world, *tan(δ)* this probably the easiest way and also the most relevant change occurring during the glass transition as it correlates the elastic and the viscous response altogether. Considering this, the T_G value for our material is 122.43°C for the first specimen and 122.12°C for the second one.

Realize that another outcome of this test has been the discovery of a secondary transition around 100°C clearly seen in the loss modulus which is the one correlated with viscosity as it represents the hysteresis losses. This secondary transition should be taken into account due to the fact that experiments around that temperature could be affected. Thus further data taken from time domain tests should be revised to see any discontinuity on the TTSP around 100°C.

We have also tried to get an analog to the time domain typical modulus from this DMA test but there is no direct relation between the storage and the loss modulus and the typical Tensile/Transverse got at tensile or even compressive tests. Actually the constant variation of

the stress at 1 Hz frequency does not allow the material to reach the maximum value of the strain. Hence the modulus has not reached the real value.

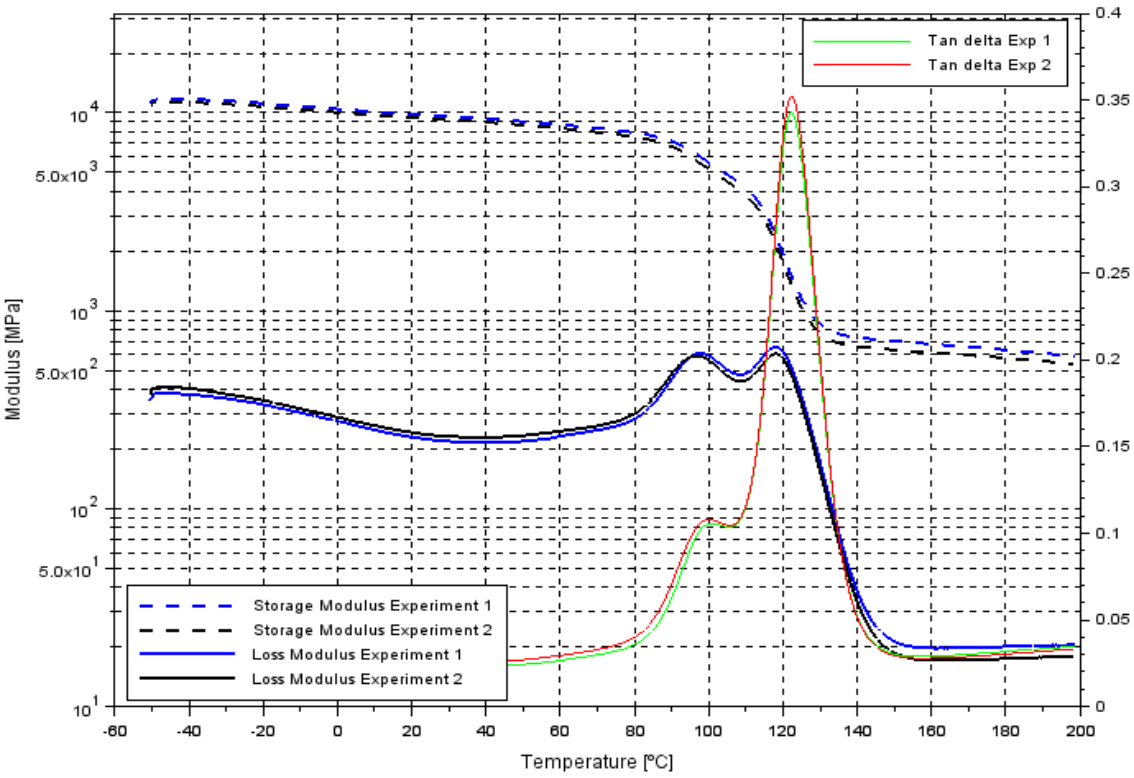

Figure 5—2. *Results of the DMA analysis of two specimens*

To summarize, our prediction of 115℃ for the glass transition temperature was surprisingly good and the results of the tests made showed a very nice agreement between the first experiment and its replica giving a final value of 122℃ for T_G.

5.2.2 Specimen preparation for Time-Domain tests

Once the DMA tests have been performed and T_G is known (≃122℃), we can move to prepare the specimens for time domain tests. As it has been explained in the introduction of this chapter, the tests will be compressive so the specimens have to be designed properly to match with this type of test. Although in literature have been found examples [2] of very long and thin specimens (similar to those described in ASTM Specification D3039-76) for creep compressive test, complex anti-buckling devices have been designed to keep those specimens completely straight and vertical in those tests. Considering that in this thesis we have focused on simpler methods that do not need such devices. In this way, cubical specimens have been chosen because of the good stability and performance they have in these kinds of tests.

In order to create the specimens we made the decision to cut them directly from the winding rotor, despite the fact that this creates additional problems such as guaranteeing the orthotropic configuration of the samples. It has several advantages as we can directly test the real composite with the real fiber density and the real cure process.

Considering that the main problem is the fiber direction should be aligned (perpendicular) to one of the faces of the cube, they cannot be very big since the fibers are curved making circles around the rotor. So the smaller the cubes are the better the consideration of straight fibers.

Furthermore, another advantage of making the specimens small is that we can get higher stresses with less driven force due to the fact that the cross sectional area is much smaller. Additionally we were informed that the machine needed to make the compressive test had a maximum driven force of 300 N and we needed to apply at least a stress of 8 MPa to the specimen because it was the prediction of the end of the linear range of viscoelasticity (around 1.5% of the compressive strength and a strain of 0.1%). In order to apply this stress level, we chose a dimension of 6 mm for the edge of the cubical specimens.

The process starts by cutting big slices from the test rim of the rotor with an industrial radial diamond saw to get pieces 6 mm thick see ***Figure 5—3***. The internal face of the rim had to be marked in order to know the fiber direction and know the orientation of the pieces; additional marks have been made to know the orientation of the little 6x6x6 mm cubes, to never lose the fiber direction reference. To get the final dimensions two more cuts must be done, but in this case with a more accurate set up and a smaller fixed diamond saw which is shown in ***Figure 5—3***. Nearing the end of this process we got aged samples which need to be reset to non aged samples.

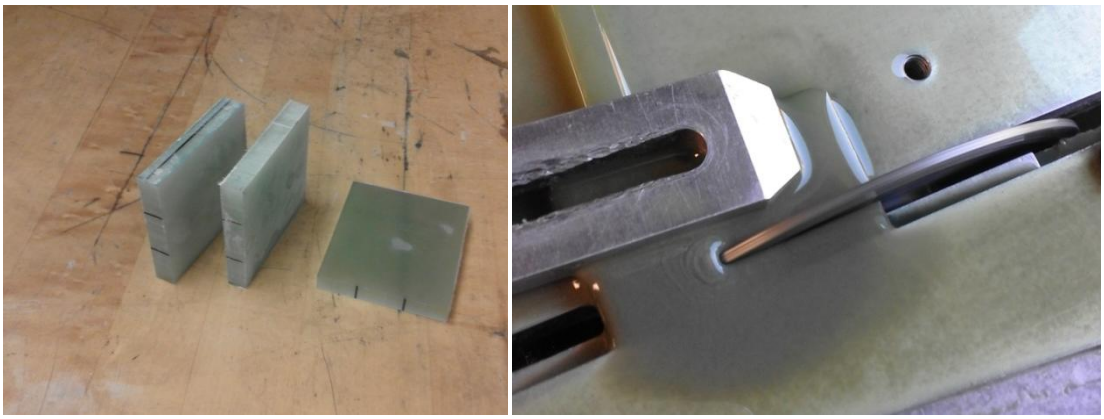

Figure 5—3. *Slices of the GFR rim (Left). Little diamond saw cutting one slice. (Right)*

A total of 30 specimens (see ***Figure 5—4***) were created this way to guarantee the stress history before the test was null i.e. we designed the experiments to use a different specimen for each one. In spite of it is possible to guarantee that the stress history is null by rejuvenating the specimens every single time after they are tested. This is very slow process that requires an amount of time we could not afford (if you want to test a one week old sample you have to have 1 week between each experiment).

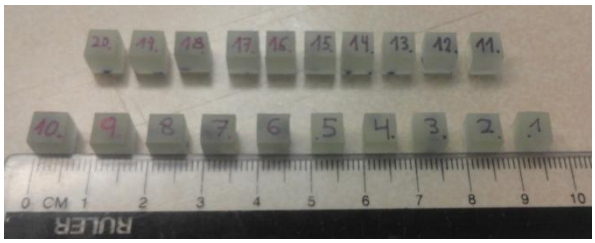

Figure 5—4. *Twenty of the specimens numbered.*

Apart from these 30 samples we created a total of six bigger samples in further stages of the project when we realized that more force could be supplied by the machine and the resolution and accuracy of the machine was not enough to get good data and smooth curves. Three of them were 10.5x10.5x10.5 mm and the other three were 14.5x14.5x14.5 mm. These bigger

dimensions amplify the absolute value of the displacement variation if the same stress is applied, specifically 1.75 times in the case of the 10.5 mm edge cubes and 2.42 times in the case of the 14.5 mm edge cubes. All of the cubes followed the same cutting process but different polishing process which will be described in the next subchapter.

Finally the last step in the specimen preparation is the rejuvenating process. This process is commonly known and it merely requires heating up the samples over T_G for thirty minutes or at least the time is needed to have an isothermal temperature inside the material you want to rejuvenate and the time the material needs to redistribute the microstructure to the highest entropy possible as it was discussed in the subchapter 3.2 (Microstructure). In our case, the age reset is carried out in an isothermal oven at 140°C (more than 15°C over T_G) during 40 minutes in order to be sure that the rejuvenation is complete. In spite of the simplicity of this step, we have to be careful with the possibility of getting moisture inside the resin while the rejuvenation is carried out. If that happens, it can invalidate the results in the time-age-dependant study.

5.2.3 Specimen adjustment

After getting data from the basic specimens we realized that the results were varying a lot depending on the sample. So as we wanted to use the specimens as they were completely equivalent some adjustment had to be performed. The two main parameters that were affecting the behavior of the compressive tests were the parallelism of the surfaces in contact with the compression plates and their own flatness as well. With the goal of deal with these disadvantages we made the decision to polish the surface until they were flat and parallel enough. However, it is not an easy task since the specimens are so small and difficult to grab with clamps or any device. This is the reason why we decided to create a specific tool to do so. ***Figure 5—5*** shows the polisher clamp (Left) we used to polish the little cubes. It has a specific height of 5.85 mm so it is perfect to reduce the height from 6.0 mm to 5.85 mm, but of course both surfaces top and bottom have to be exposed to the sandpaper, to do this, we elevated the clamp 0.07 mm with a flat thin sheet of aluminum over the table surface and after that we installed the cube at the end of the clamp laying on the flat table.

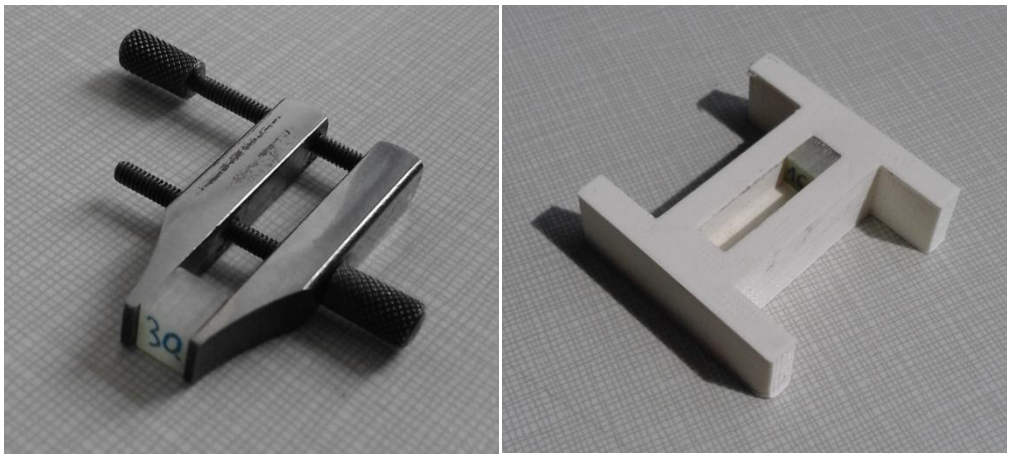

Figure 5—5. Polisher c*lamp (Left). 3D printed polisher prototype (Right).*

We also used the prototype shown in ***Figure 5—5*** (Right) with several steps on the slot to polish the specimens in several stages. Unfortunately some of the cubes were too big for the slot and

others were too small. Furthermore it had no clamping system so it was not the best design for the polisher we wanted.

5.2.4 Sample Measurement and Quality

In order to see the quality of the specimens, 8 measurements have been taken with an electronic caliper from every dimension. Essentially we have measured each edge of the cube twice waiting one day to do the replica. We have in total 24 measurements per specimen so we could know how good the measurement method was and also how parallel the surfaces are. Despite the fact that each dimension could have different standard deviation of the repeatability, we have assumed that the error made is following the same curve "Normal law" We can assume this considering that the same person did the measurements with the same instrument using the same method. With this assumption we can get the accuracy of the measurements using Eq.23 and thus the accuracy of the cross sectional area value obtained as shown in Eq.24.

$$\sigma_{\text{mean}} = \frac{\sigma_{\text{repeatability}}}{\sqrt{\text{number of measurements}}} = \frac{0.038}{\sqrt{8}} = 0.014 \text{ mm} \qquad \text{(Eq.23)}$$

$$\sigma_{\text{area}} = \sqrt{{\sigma_{\text{mean}}}^2 + {\sigma_{\text{mean}}}^2} = \sqrt{2} \cdot \sigma_{\text{mean}} = \sqrt{2} \cdot 0.014 = 0.019 \text{ mm}^2 \qquad \text{(Eq.24)}$$

Furthermore, we calculated the parallelism of the specimens with our own made variable called Parallelism Deviation (*P.D.*) using the deviation of both height and width and choosing the minimum value of those so it follows the Eq.25. We used the minimum of those values because despite the fact that the material is orthotropic, two of its principal directions are supposed to behave exactly the same. Thus we chose the best dimension to fit in the test. It is interesting to realize that we can use the same value for an approximation of how bumpy or non-flat the surfaces are.

$$\text{Min (P. D.)} = \frac{\text{Min}\left(\sigma_{\text{height R1}} + \sigma_{\text{height R2}},\ \sigma_{\text{width R1}} + \sigma_{\text{width R2}}\right)}{2} \qquad \text{(Eq.25)}$$

Specimens with height as best dimension are 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 19, 20, 21, 22, 24, 25, 26, 30 and specimens with width as best dimension are 1, 2, 3, 5, 18, 23, 27, 28, 29. There are more specimens selected as height because in order to mark height or width a visual inspection was made and we tried to use the best dimension as height for practical reasons. But after the measurements we realized that some of them were not chosen correctly so we marked the direction of the compression with permanent pen.

Table 5-2, ***Table 5-3***, ***Table 5-4***, ***Table 5-5*** display all the values of the dimensions of all the specimens used, the values correspond to the mean of the 8 measurements made, considering that we assume that the maximum error made is equal to 2σ (Confidence interval of 95%). Hence length, height and width have ±0.027 mm and the error for the area is ±0.038 mm^2.

Prop\Nº Sample	1	2	3	4	5	6	7	8	9	10
Length sample mean (mm)	6.12	6.02	6.08	6.05	6.03	6.08	6.14	6.03	6.03	6.14
Height mean (mm)	6.17	6.17	6.22	6.08	6.26	6.11	6.07	5.93	6.17	6.20
Width mean (mm)	5.84	6.03	6.14	6.09	5.98	6.01	6.04	6.22	6.15	6.21
Area mm^2	35.76	36.29	37.33	36.83	36.03	36.50	37.10	37.49	37.09	38.14
Min Parallelism Deviation	0.013	0.020	0.010	0.019	0.017	0.028	0.046	0.015	0.019	0.016

Table 5-2. *Specimen 1-10 dimensions*

Prop\Nº Sample	11	12	13	14	15	16	17	18	19	20
Length sample mean (mm)	6.13	6.08	6.10	6.04	6.04	6.07	6.03	6.05	6.03	6.03
Height mean (mm)	6.15	5.88	6.18	6.10	6.16	6.14	6.18	5.67	6.02	6.06
Width mean (mm)	6.07	6.28	6.26	6.27	6.19	5.88	6.17	6.11	6.13	5.76
Area mm^2	37.21	38.16	38.18	37.87	37.42	35.71	37.21	36.96	36.94	34.71
Min Parallelism deviation	0.012	0.015	0.014	0.006	0.012	0.011	0.015	0.010	0.011	0.025

Table 5-3. *Specimen 10-20 dimensions*

Prop\Nº Sample	21	22	23	24	25	26	27	28	29	30
Length sample mean (mm)	6.06	6.06	6.03	6.06	6.02	6.03	6.02	6.03	6.04	6.09
Height mean (mm)	6.09	5.91	6.02	5.87	5.85	5.93	5.99	6.53	5.91	6.10
Width mean (mm)	5.70	5.83	5.89	6.00	6.06	5.88	6.05	5.98	6.08	5.85
Area mm^2	34.5	35.3	35.5	36.3	36.5	35.4	36.4	36.1	36.7	35.6
Min Parallelism deviation	0.009	0.004	0.019	0.004	0.005	0.012	0.021	0.013	0.013	0.014

Table 5-4. *Specimen 20-30 dimensions*

Prop\Nº Sample	31	32	33	41	42	43
Length sample mean (mm)	10.56	10.00	10.63	14.64	14.87	14.81
Height mean (mm)	10.48	10.83	10.64	14.56	14.25	14.45
Width mean (mm)	10.87	10.86	10.82	14.60	14.93	14.80
Min Parallelism deviation	0.021	0.010	0.06	0.028	0.010	0.059

Table 5-5. *Additional specimens 31-33; 41-43*

In summary, a considerable number of measurements have been carried out in order to get more precise results and to be able in further stages of extracting conclusions from the experimental results. Although initially they had an accuracy purpose, at the end these measurements have provided a good explanation of the stiffness variation perceived in the following chapters.

5.3 Design of Experiments

5.3.1 Time-Temperature Superposition Experiment

Once the samples have been made and measured properly and the experiments have been designed the TTSP experiment can be done, a specific machine has been used. Even though at the beginning of the experimentation an alternative machine from the same company was

used (*Electroforce® 3200*), it presented several problems that we couldn't fix after several weeks so we decided to move to the other model, called *Electroforce® 3510* from BOSE Company. The machine's specifications appear in ***Table 5-6***. The accuracy of the model used is less than "*model 3200*", however it is considerably bigger, it can apply much more force, and the problems with vibrations we had disappeared. Furthermore, the vibrations problems made the specimen move from its position and it produced a sharp noise that was very unpleasant and indicated something was wrong.

To solve these problems we tried to tune the machine, filter the high frequencies and 50 Hz from electrical grid, block one of the two axial powers, change the specimen size and material, and other recommendations in [12] and [13] but none of these seemed to solve the vibration problem. Additionally we tried a very low stress experiment in which the vibration was minimal to see if the creep was observable even at low stress ranges, but the response of the material over 4 hours showed other effects than creep. This could be due to the heating of the sensors generated by the low vibration or other thermal associated errors, but the fact was that the opposite behavior from the expected was shown thus we gave up on this machine and started with the bigger model (*model 3510*) which actually provided us reasonable results from the beginning.

	Max	Resolution	Max deviation	Controller	Sensor
Force Compression	7500 N	0.1 N	0.06%	Electromagnetic	Load Cell
Force Tension	7500 N	0.1 N	0.23%	Electromagnetic	Load Cell
Velocity	± 1.5 m/s	0.025 µm/s	-	Electromagnetic	
Frequency	±100 Hz	0.00001Hz	-	Electromagnetic	
Displacement	±25 mm	1 µm	0.06%	Electromagnetic	
Temperature	60°C	0.1°C	0.06%	Electrical Resistors Water Heating Plates	Fowler MkIV

Table 5-6. *Electroforce 3510 specifications* [14].

Considering the machine changed, the whole experiment design had to be changed as well because more force can be applied now and less accuracy implies we need more creep to happen. Assuming the response is linear Eq.2 is right. Thus increasing the stress applied the creep response is multiplied by the same factor i.e. we have to increase the stress to see more creep. Moreover, the temperature range to do the study also had to be redesigned because of the heating method, it changed from a convection oven to a water bath so less temperature range is possible with it. Of course it is not possible to heat the water bath over 100°C but the max temperature in this case was much lower (60°C) as it is shown in ***Table 5-6***, this is because the heating power of the Heating Plates installed was not enough to provide more temperature in a huge water bath designed by BOSE company. This is an inconvenience but as no other machines were available, we performed the experiments with it.

The new experiment design is shown in ***Table 5-7*** in which the maximum temperature is way below the T_G. However the TTS principle should be applicable in a shorter range of temperatures i.e. despite that the response is less reliable in long the term it should be able to

make predictions. In this case all the experiments should have the same age which it has been chosen at 168 h which corresponds to 1 week for practical reasons.

Nº Sample	1	2	3	4	5	6	7	8	9	10
Previous Temperatures	30	40	50	60	70	80	90	95	100	110
New Temperatures	23	25	30	35	40	45	50	55	57	60

Table 5-7. *TTSP experiment design, Range of temperatures.*

The age should be enough to satisfy the snapshot condition expressed in Eq.26 where t_e is the age and λ is the test duration, this way you guarantee that during the test the aging of the material is negligible i.e. it has a practically constant age. Moreover one week old specimens are considerably less stiff than older materials, at least theoretically thus one week is enough to satisfy the snapshot condition but at the same it presents a relatively short time in order to rejuvenate the specimens. Finally, the test duration of the experiment has been chosen as 2 hours and the all samples dimensions picked as the small cubes as we have enough of them to do all ten experiments.

$$\lambda < \frac{t_e}{10} \qquad \text{(Eq.26)}$$

For this Time-Temperature experiment and for the whole study we have calculated the compliance from the stress and strain data, compliance has de advantage of being independent of the size of the specimen and independent of the level of stress applied. Compliance is defined in Eq.27 where strain is measured in % and σ is measured in [GPa], so compliance units are expressed in [GPa^{-1}]. From it we have built compliance curves against time. Were the measures of the time are recommended to be taken equally distributed in log(time) scale. Unfortunately the *Electroforce 3510* take the measurements automatically and equally distributed on linear time scale, moreover the number of measurements made can be as big as one wish so this issue is not a particular problem.

$$\text{Compliance} = \frac{\varepsilon(t)}{\sigma} \qquad \text{(Eq.27)}$$

Summarizing, the design has been changed to satisfy the news specifications of a machine, and long term predictability has been compromised, but the main idea of the study remains the same. However in the next chapter we are going to discuss the results and the data processed to conclude that the amount of creep observed is much less than expected and then the machine's accuracy is not enough to carry out this TTSP experiment design.

5.3.2 Aging Experiment

Considering that the Age-Time experiment involves the time and that all the specimens are tested under different ages; these tests require more planning and the rejuvenating day and time have to be scheduled as well. In the table ***Table 5-8*** the age and the test duration for each specimen are shown, the test duration should satisfy the snapshot condition explained in the previous subchapter (see Eq.26) in order to neglect the aging during the experiment. In the age experiment all the variables but the age of the specimen and test duration should remain constant, so the temperature has been chosen as the maximum allowed by the testing

machine (60°C) to evidence the maximum creep possible, and finally the stress level applied is 8 MPa.

Sample	11	12	13	14	15	16	17	18
Age [h]	2	4	10	24	48	96	144	192
Test duration [h]	0.2	0.4	1	2	3	4	6	8

Table 5-8. *Aging tests specifications*

Additionally, ***Table 5-9*** shows the schedule for the experiments. The longer is the duration of the test, the less tests can be done in the same day so the whole experimentation requires at least 4 days for each replica. This way the minimum time needed between replicas is 4 days in the case that the same specimens are used to do the replicas (and it is recommended otherwise they may have a variation), in the case of having different specimens you don't need to wait any time so it is possible to start the next replica the next day.

Day\Order	1	2	3	4
4th	11	12	13	14
3rd	15	16	-	-
2nd	17	-	-	-
1st	18	-	-	-

Table 5-9. *Experimental order for the Time-Age Test*

5.3.3 Linearity Test

As it is mentioned in chapter 3, we have assumed that our material is linear or at least our measurements are within the linear range. To check if that assumption is valid a linearity test has to be done. In this case we try to confirm the Eq.2 which states that the stress level applied and the compliance in the creep test are proportional. Thus different stress levels are applied with constant Temperature (60°C) and constant age of 1 week. Five experiments with three replicas should be enough to determine whether there is linearity or not.

Nº Sample	19	20	21	22	23
Stress scaling (MPa)	2	3	5	7	8

Table 5-10. *Properties of Glass Fiber reinforced epoxy Composite.*

5.3.4 Parallelism Test

After the measurements of the specimens and the calculations of the parallelism were completed, we concluded that short parallelism tests could be performed. The idea behind is to see if there is real correlation between the results and this number we have used to quantify the Parallelism. To do so we needed to carry out several experiments with the exact same conditions but changing the specimen each time. Of course in this case, it is especially important to compute the values of the dimensions of each specimen.

Furthermore, the replicas can give a representative idea of the error made because of changing the specimen.

6 Data Analysis

In this chapter all the data collected from experiments is displayed, processed and analyzed, to do this we have used the free software *Scilab* which has been really helpful in order to do all the operations required to the data and in order to process an optimal way and fully automatic. Moreover this tool we have created can help to speed up further researches with similar machines and tests.

6.1 Software

We have created a tool in order to accelerate to process the data, this tool is developed in Scilab code and split in several scripts functions and coordinated by one single script where there are the variables to change for different processes and results.

The creation of this tool is remarkable because of the large quantities of data we got that is more than 50 total experiments. Each of them with thousands of measurements of 6 variables: *Time, elapsed-Time, Load, Displacement, Axial command* and *Temperature.* Some of them could be interrelated as Temperature and Axial command with Load and Displacement. As such, this tool allows enabling or disabling these correlations and show the result in the plots of the graphs. Furthermore, this tool calculates the compliance as it has been explained in the previous chapter (see Eq.27), it can plot compliance curves with different tests duration, making the mean of hundreds of points to collapse one curve with many points to a reduced one. Making the mean of points has been one of the keys to visualizing the results due to the fact that the resolution of the testing machine is so low that you can only see few discrete steps in one hour test, however the real value of the measuring point is in between the two oscillating numbers we got at each second. So the more points we use to make the mean, the better the value is going to be calculated, but less points can be represented in the graph which is not a big deal since we have thousands.

Another feature of this program is that you can enter the numbers of the tests you want to visualize and it does all the steps for each test including the minimization of error by least squares of the exponential laws the curves should follow. It can visualize up to 10 curves at the same time including their exponential fit. Furthermore it has been designed for picking the information from ".txt" files with the row data in columns, and the name of the file is used to create an automatic legend for the figure.

Despite the Scilab's scripts being the base for the explanations, all the experiments have been checked while they were running with *WinTest® Software*[13], which is the tool BOSE Company provides to analyze the live results. This has been especially helpful to let the variables to stabilize before the tests were conducted.

Finally, it has a file where all the information about the tests is unified, in this way all the names of the files, the number of the experiment they correspond and the number of the specimen used are stored. This information allows the program to calculate the compliance automatically even though all the specimens have different dimensions values.

6.2 Analysis

In this subchapter we analyze the results produced with the procedures explained in *5. Experimental Data Acquisition*. Material behavior is explained and also phenomena related to the testing machine has been observed and discussed. Moreover not every procedure's design in the previous chapter has been conducted due to several unexpected behaviors.

6.2.1 Pre-Analysis

Considering the "Parallelism deviations" described in *5.2.4. Sample Measurement and Quality,* a pre-analysis was conducted to see if there is real correlation between the results and this number we have used to quantify the parallelism. The results show that indeed there is correlation between the results and the calculated "Parallelism".

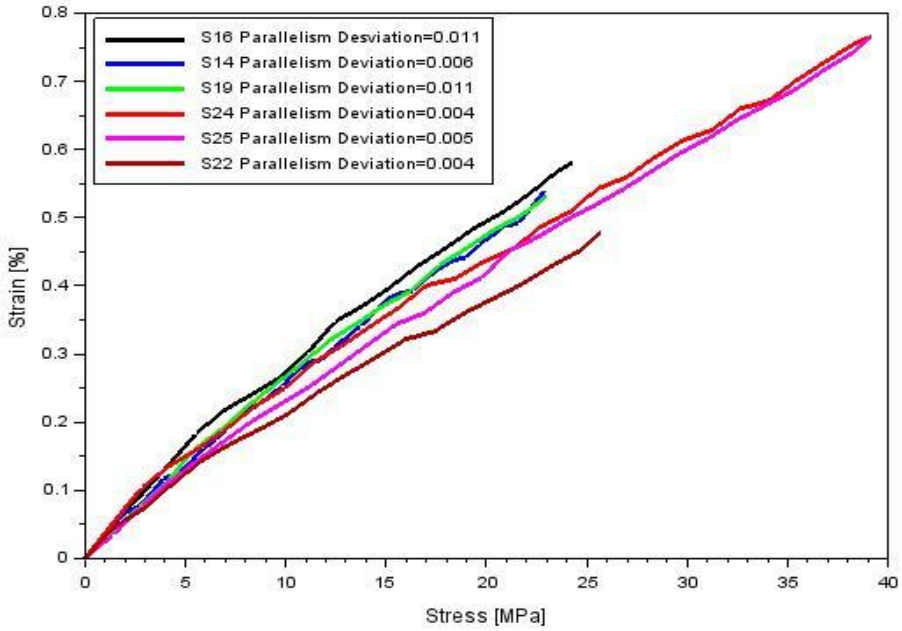

Figure 6—1. *Strain-Stress compressive curves of Specimens 16,14,19,24,25,22.*

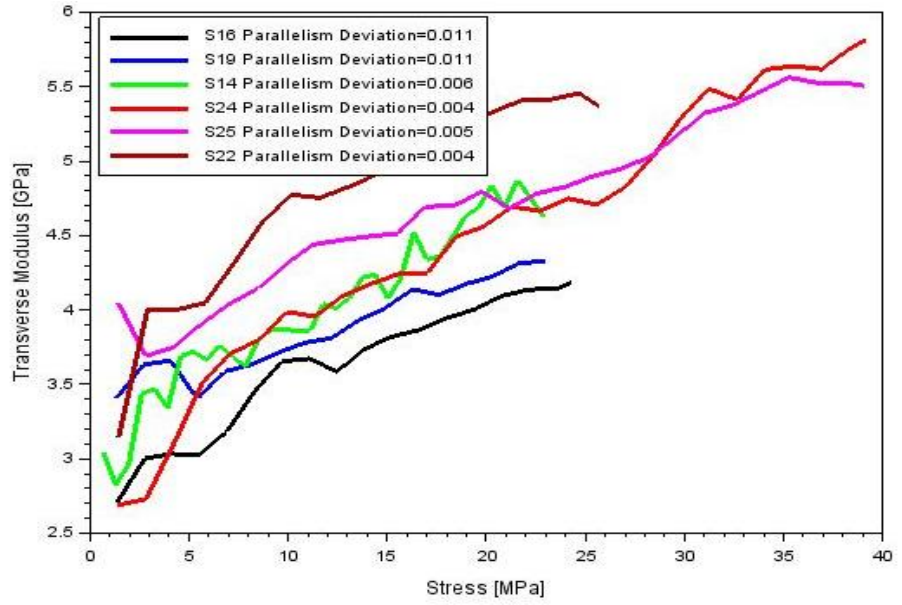

Figure 6—2. *Transverse compressive modulus of Specimens 16,14,19,24,25,22.*

In ***Figure 6—1*** and ***Figure 6—2*** the results from a typical Modulus Test are shown. Displayed in two different ways, the first one corresponds to a stress-strain and the second to a modulus against stress graph which ideally is completely flat if the material is linear but in this case it is certainly not. This could be explained by two different theories. The simplest is that the material is not linear, however it could be explained by the fact that the contact surface increases with the Stress applied due to irregularities in it. Nevertheless, there is a clear fact that the stiffest specimens corresponds to the flattest ones, as you can see comparing the "*Parallelism deviation*" of all the samples. Thus the data validates in this case the variable used to describe this phenomenon at least qualitatively.

The conclusion we made is that it is better to use the best specimens in terms of parallelism to carry out the experiments and also that the deviation is unexpectedly huge (reaching the 20% in the worst case).

6.2.2 Order of Magnitude for aging

Considering the low resolution of the *Electroforce 3510* testing machine, we made tests for the order of magnitude of the different variables we wanted to quantify at the first place i.e. instead of going for the designed experiments we first wanted to guarantee that the behavior of the material had the expected tendency.

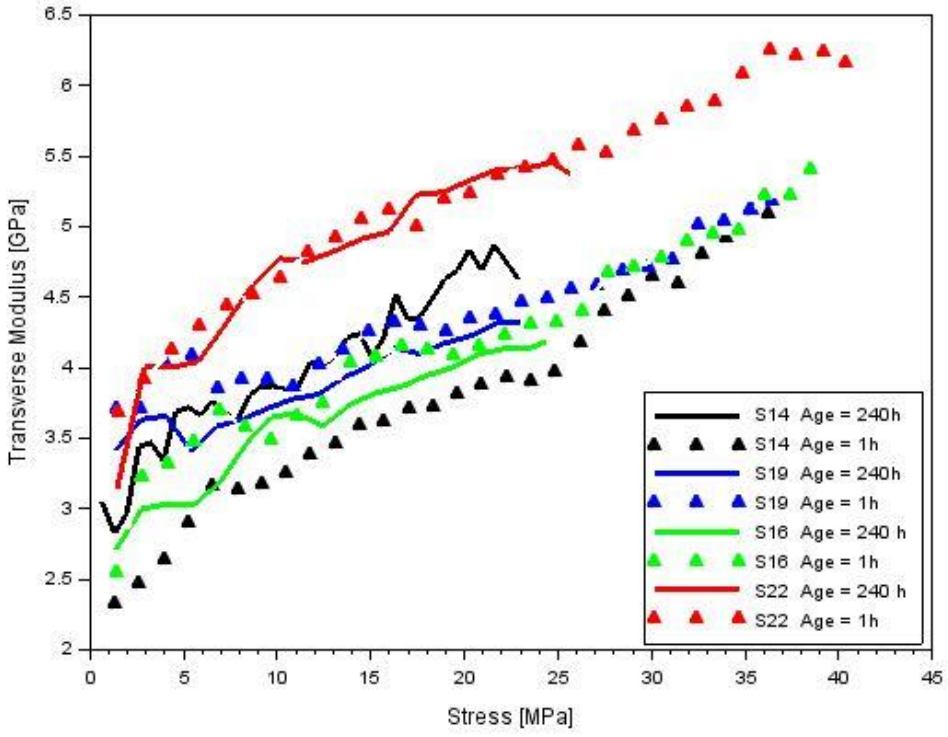

Figure 6—3. *Transverse Modulus (Compressive) vs. Stress. Aging effect.*

In this case, like the *Pre-analysis* we have measured the stiffness of the material in a short test instead of the compliance in a long creep test. This way more data can be collected to comparisons. As we have seen before, the specimen makes a huge difference in the values of the stiffness but the repeatability of each specimen is good. As such, in order to compare the aging effect we are going to observe only the evolution of a single specimen when rejuvenated i.e. there is no comparison between the whole set of specimens among them.

In ***Figure 6—3*** the results are displayed, in a solid line the 10 days old (240 h) material, and in triangles marks, the rejuvenated specimen (≈ 1 h). Different colors show different specimens tested. The results are difficult to discuss because apparently there is no correlation between the age and the Modulus. On the one hand the curves of the specimen 22 (red lines) seems to be overlapping and no substantial change is seen. On the other hand specimens 16 and 19 (green and blue respectively) have an observable change, but is contrary to the expected, it seems that the modulus (and hence stiffness) has slightly increased. However, this behavior does not conclude that the creep is lower in these cases but it does demonstrate that the stiffness has not decreased with the rejuvenation. Finally the specimen 14 behaves differently, in this case the modulus have changed considerably and in the opposite direction. Therefore we can conclude that there are other variables which are interfering with the experiment that we have not yet considered such as humidity or sensor stabilization which could explain why the first experiment of the day provide weird results compared to the rest of experiments because in this case the first is the specimen 14.

In summary, the results of this experiment show that there is no direct correlation between stiffness and age, or at least it is so small that it is hidden by other unknown parameters.

6.2.3 Repeatability

Once we have observed the large variability between the responses of different specimens, we have conducted tests of repeatability to ensure the variability is not due to the machine but to the parallelism. In ***Figure 6—4*** it is shown the transverse modulus of two different specimens tested 4 different days. It shows a considerable variation with a maximum value around 10%.

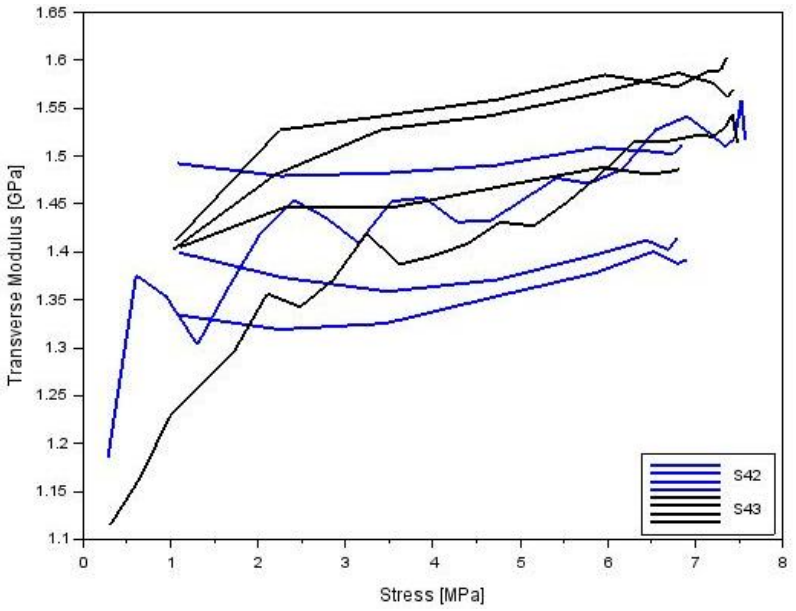

Figure 6—4. *Stress vs. Transverse Modulus. Specimen 42 and 43.*

The next step was to perform a repeatability test for the creep response as well, in this case we got a pair of curves for three different specimens, the results are shown in ***Figure 6—5*** where the specimens 43 and 42 give certain good repeatability but the response of number 32 is simply too different to be considered as reasonably. We don't have any clue about what happened in that case but it shows that many parameters take place together and this kind of compressive creep test is very complicated to be performed with the testing machine we had.

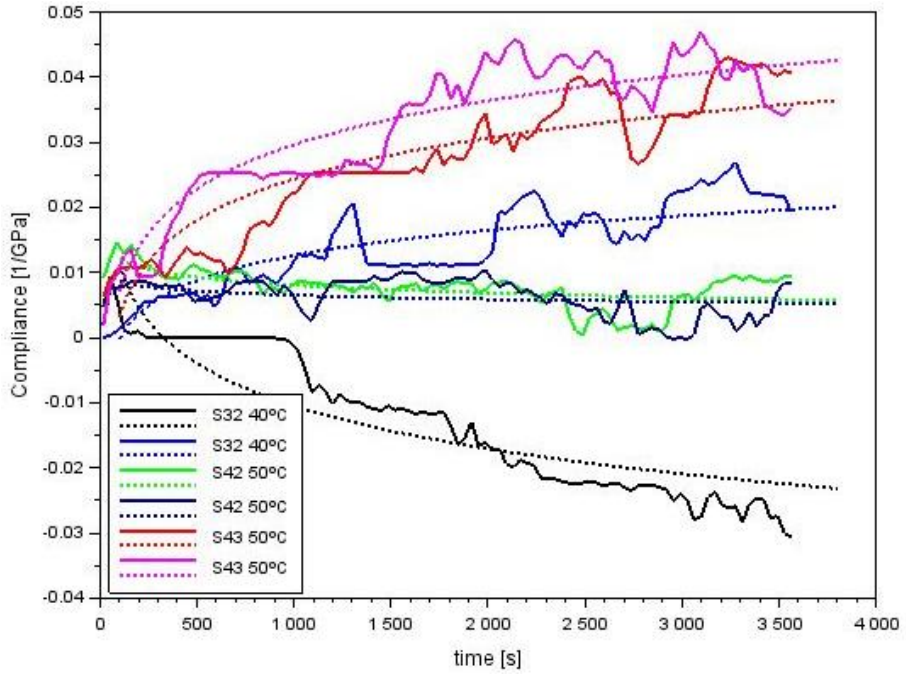

Figure 6—5. *Repeatability of creep test.*

6.2.4 Sample Size

Considering the problem of the parallelism deviation we tried several ideas to get better results but basically the two more relevant ones are: first scaling the cubes to reduce the relative error and second to polish the surfaces in order to get more parallel surfaces, which is explained in the chapter *5.2.3 Specimen adjustment*.

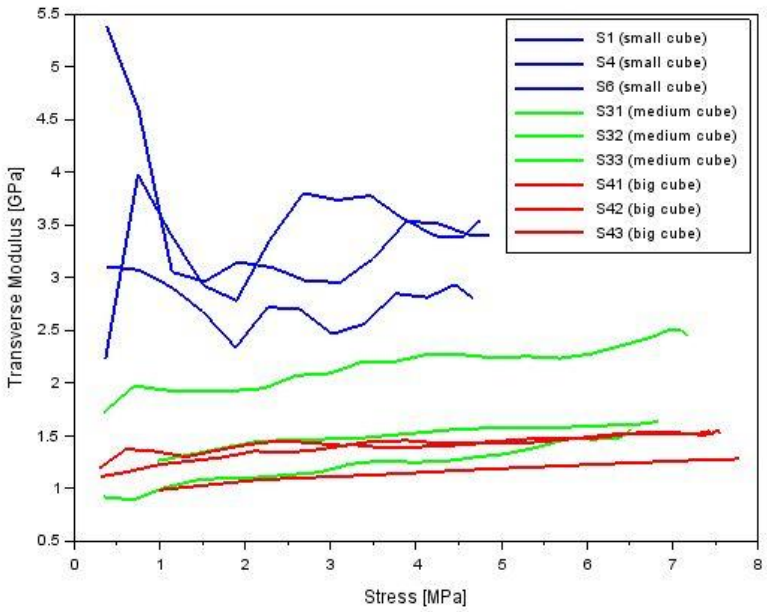

Figure 6—6. *Comparison of Transverse Modulus (compression).*

The polish procedure was not completely successful in making the samples more equal, and the sizing trial was even worse considering that the more relevant factor when compressive tests were made was the size of the specimen which shouldn't be, in fact as the material is exactly the same, the modulus shouldn't depend on the size at all but the results, which are

displayed in ***Figure 6—6***, show enormous discrepancy between small, medium and big specimens.

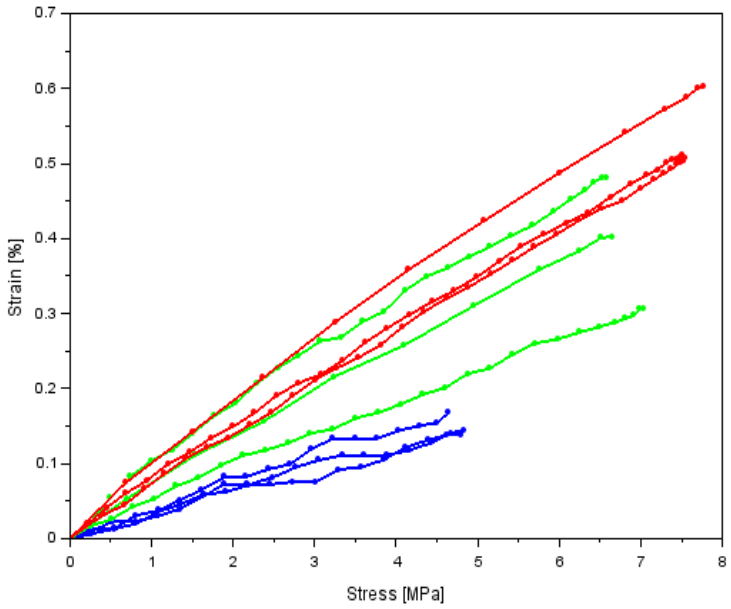

Figure 6—7. *Stress vs. Strain curves (same data as previous Figure).*

This is not encouraging at all, however at least there is a tendency to the modulus to be more stable the bigger are the cubes tested. This demonstrates that the idea of making bigger specimen actually worked because the relative error committed was less considering that more force is needed to apply the same amount of stress i.e. In ***Figure 6—6*** and ***Figure 6—7*** the smaller cubes were tested up to 300 N, the medium cubes at 900 N and the big cubes at 1800 N.

6.2.5 Dilatation test

Considering that the experimental method to see the creep response is based in a water bath set up, we found interesting to see the dilatation of the submerged parts of the testing machine with a specimen in. This gives us an idea of the dilatation which, even being in an order of magnitude of few microns, could be very high compared to the creep.

The results in ***Figure 6—8*** showed a perfect agreement between the shape of the temperature and the shape of the displacement during this test that last for more than three hours. The test was carried out applying a compressive constant force of 10 N to guarantee the contact between the specimen and the compression plates and then the displacement was measured while varying the temperature. This experiment last for so long (more than 3 hours) because of the time needed to change the water bath temperature is huge, the main advantage of the bath is that the temperature last very long to change and hence the value is very constant.

$$\alpha = \frac{\Delta\varepsilon}{\Delta T} \qquad \text{(Eq.28)}$$

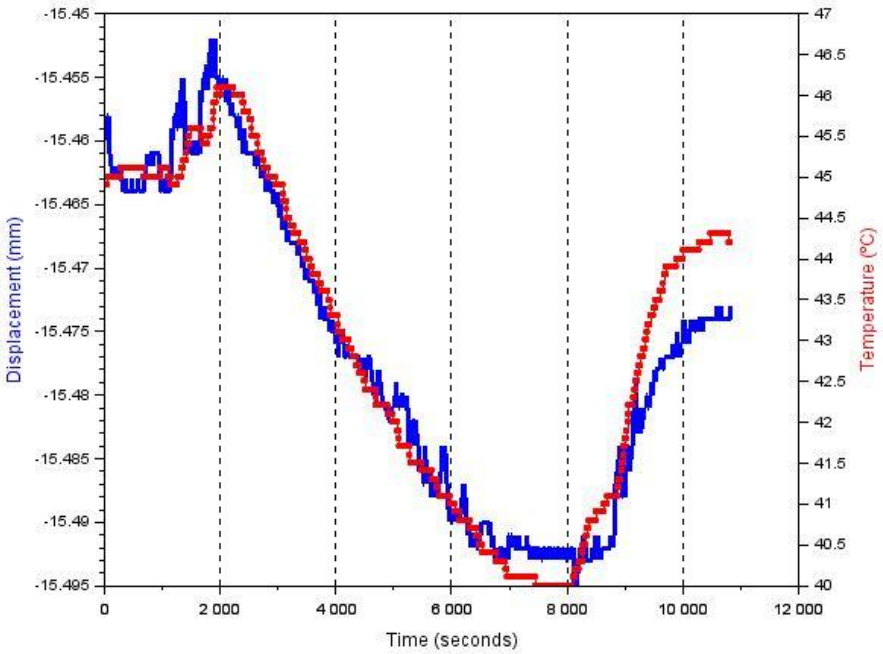

Figure 6—8. *Relation between the Temperature and Displacement (Dilatation Test).*

Furthermore this data allows doing a prediction of the dilatation constant "*α*" using the Eq.28 which can be used for correcting the values obtained in the creeping tests, having *Δε=0.04 mm* and *ΔT=6°C*; the value of the expansion constant is *α=6.7 μm/°C* .This is no negligible even with the water bath in which the maximum variation expected is ±0.2°C. With *α,* it has been possible to recalculate all the results and re-plot all the curves obtained in order to consider dilatation. However it didn't improve the shape or the repeatability of the curves, so all the graphs showed are actually calculated without the expansion correction.

6.2.6 Creep Tests

Once the possible errors for the study are known, we started the creep tests, which are supposed to give us the real information about viscoelasticity and hopefully enough information to create the model we discussed in the *chapter 4.* Unfortunately, all the errors found in all the previous tests are hiding the real creep as we discover it its very small compared with any other parameter.

First, the efforts went to find out the correlation between the temperature and the time but considering the results were not concluding we start putting effort in solving the accuracy problem, for example: correcting the dilatation, polishing the specimens, applying the *Parallelism deviation* as a correction factor, increasing the size of the cubes to reduce the relative error, applying cyclic loads previously to the tests and so forth so on. These considerations have been discussed through the thesis extensively, and the final conclusion we can extract is the needed of a more accurate machine, or even better, building an own design set up for this particular tests.

In doing these tests, we had to discard the first test of the day in every case because some unknown factors such the machine is not at completely thermal stationary (probably the electromagnets) were affecting the results too much, most of them even show a big material recovery but under this stress is obviously physically impossible for the material to recover.

This behavior is shown in ***Figure 6—9*** where almost all the curves are flat or even recovery is seen (Negative Compliance).

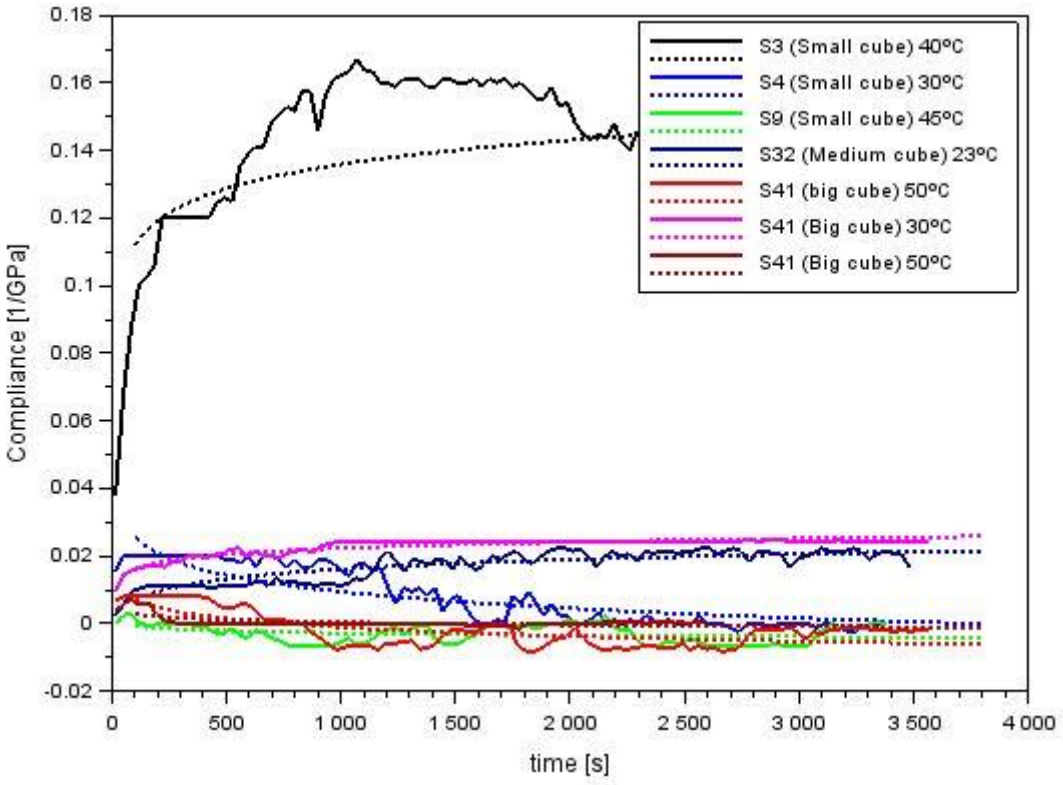

Figure 6—9. *Creep of the first experiment of different day.*

There are few curves that present a reasonably creep behavior, this could be the cases of *S41-30°C*, *S32-23°C* and *S3-40°C.*The first case and the second one, could be because of the low temperature of the tests, we have observed that when the tests were performed at room temperature this effect of "*the first of the day"* didn't happen. And the case of the Specimen 3 is weird itself because it presents even more compliance that other further tests performed at 20 degrees over that temperature. Apart from these three exemptions (which aren't exemptions really) all the rest behaves abnormal, this is why we have discarded all of them from the evaluation of the creep.

On the other hand, the creep curves of the rest of the tests (those which aren't *"the first of the day"*) seem to represent the real behavior of the material even though the machine doesn't provide us smooth results because of the resolution it has. In the ***Figure 6—10*** it is shown the first sweep of temperatures using the small cubes, it goes from room temperature (23°C) in which the water bath was not used up to 57.5°C in which the heating plates were at its maximum capacity (so the bath can't heat above that temperature). All the specimens were compressed with a load of 300 N which gives an approximate stress of 8 MPa depending on the exact size of every cube, but the Compliance as a variable is independent of size and stress so the results are automatically corrected when the compliance is calculated using the real size. This curves show that there is some correlation between the temperature and the creep behavior but again, the resolution and the specimen factor play against us so as all these experiments were done using different specimens (in order to have the same age for all of them) some of the curves are place in the wrong position, for example the 57.5°C curve (red)

should be slightly over the 55°C curve (hard blue) and 40°C curve (blue) is far from the its theoretical position in between 23°C and 50°C. However we can conclude that the creep is happening excluding the first of the day because it doesn't have a good conditioning.

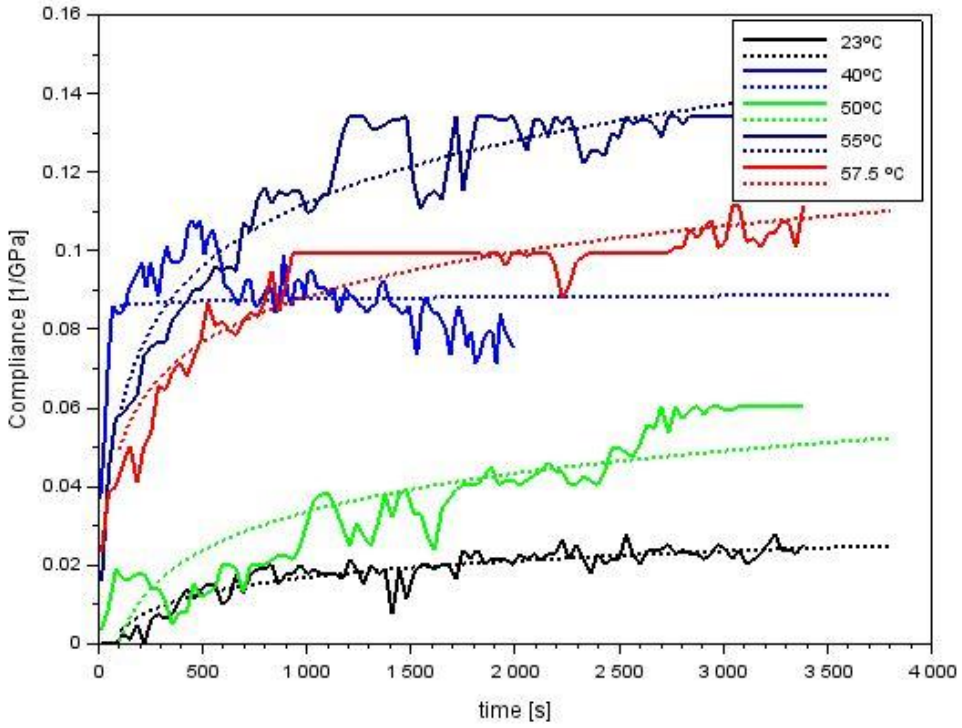

Figure 6—10. *Creep curves at different temperatures.*

From these curves is tough to found the parameters discussed in *chapter 4* due to this big specimen dependency. We came up with the idea of using the parameter "*parallelism deviation*" for adjusting the curves, it might have a direct relation but it would be the very last resource.

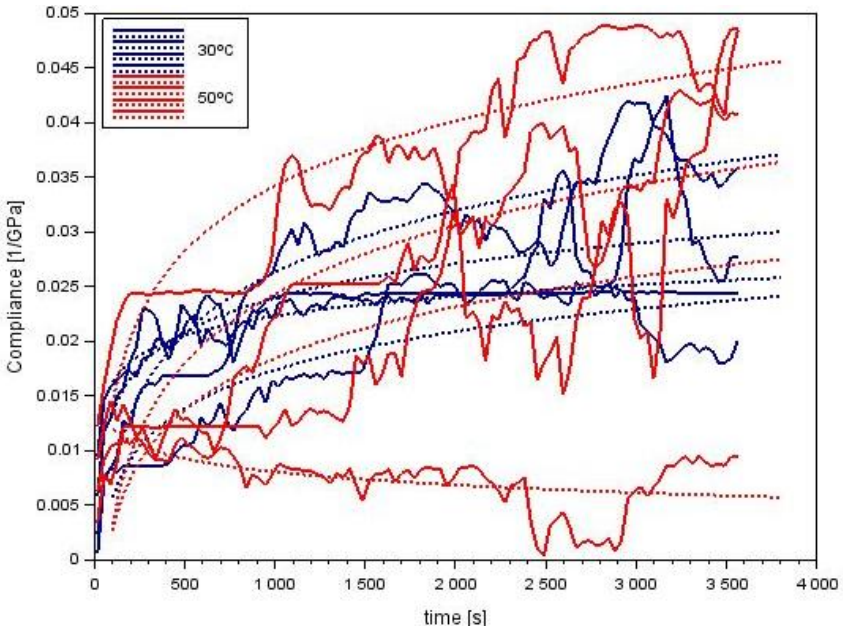

Figure 6—11. *Creep response at two different temperatures, 30°C and 50°C.*

Moreover the repeatability test showed in previous subchapter gives us little hope to apply that idea due to the fact that the error seem to come from a lot of unknown parameters which we have no clue about i.e. even with the same specimen and the same experiment the results are very different in some cases.

Considering this, it would be more reasonable trying to see the difference of the creep at two different temperatures and repeat it for many specimens to see if the tendency is real. To do so we have performed eight tests, four of them at 30°C and the rest at 50°C. This was done in two different days to let the specimens to recover during the night so the same four specimens tested at both temperatures. In ***Figure 6—11*** the results are displayed, in red the 50°C curves and in blue the 30°C curves. This test unfortunately shows that temperature is not correlated to the creep thus contradicts the previous results (in ***Figure 6—10***). Furthermore at lower temperature it seems the data appears more stable but it is not conclusive.

The initial goal of correlating the creep and the temperature using the TTSP hasn't been reached by the use of this machine despite a lot of effort was made to aisle the main factor causing the error and the variance, this doesn't mean that the correlation is inexistent but using the experiments made is not possible to find it out.

6.2.7 Recovery Tests

At the very beginning of the experimentation, the observation of the big deviation of the results and the hence the bad repeatability the tests had, we started to get the data of the next 20 minutes after the compressive test was done, this way we can get information about the recovery of the material, the idea behind is to see if we can get better results from the recovery, and as it is an equivalent to the creep, it should allow us to get the parameters of the TTSP that we were looking for, moreover the recovery was done at very low stress (close to zero) just the necessary to guarantee the contact between the compression plates and the specimen and hence have a good measurement of the displacement.

Unfortunately we got similar results to the previously obtained, they are shown in the ***Figure 6—12*** which is the comparison between the specimens at 30 and 50 degrees they show the recovery of the specimens after the tests in ***Figure 6—11*** in other words, the recovery after 1 hour at 8 MPa, for this tests we recorded the first 20 minutes due to the fact that it was a side experiment and otherwise there were no time in one day to get enough relevant data. The ***Figure 6—13*** shows the recovery at the same conditions as the previous figure showing the response of specimen 31 at different temperatures, as we found in the creep, the recovery was also unable to make a good agreement between temperature and compliance. However the results are significantly similar, in other words, the order of magnitude for the creep and the recovery is very similar considering the big deviation, notice that we can affirm this at least within the first 1200 seconds, Thus this actually allows us to validate the creep as a phenomena that is occurring, if no recovery was observed then the "creep" seen would actually be plasticity instead of the viscoelasticity we were looking for.

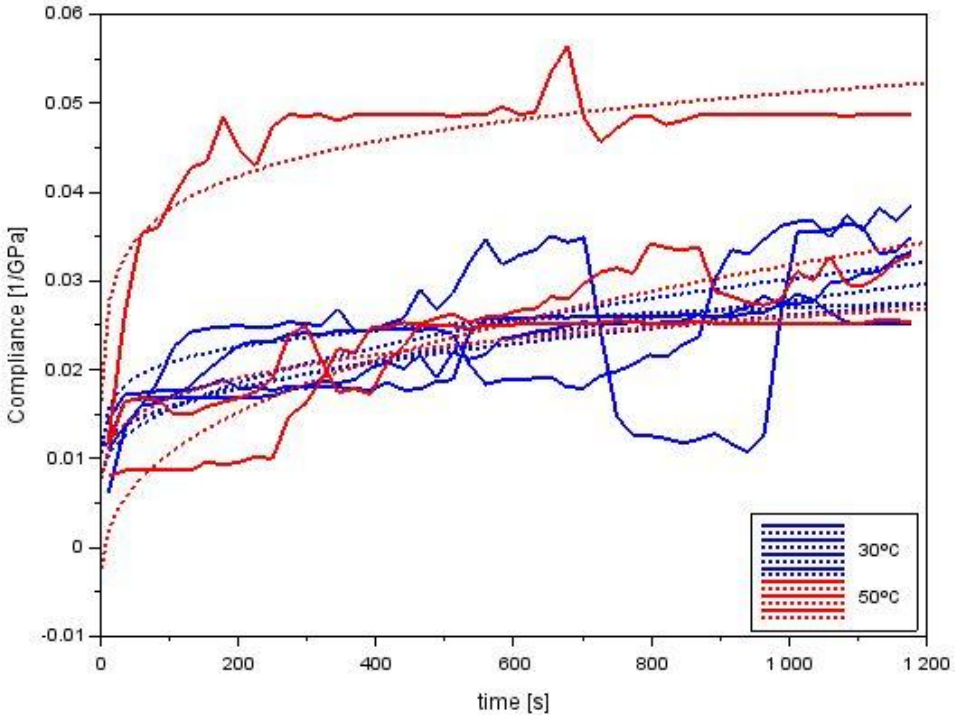

Figure 6—12. *Recovery response after 1 h at 8 MPa. Comparison 30°C-50°C.*

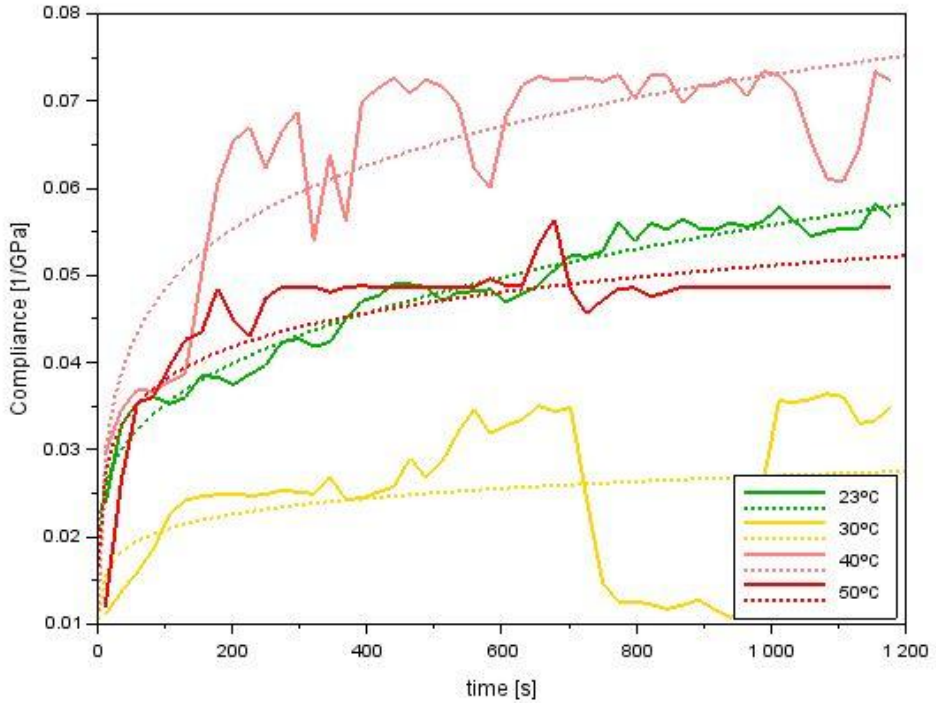

Figure 6—13. *Recovery response after 1 h at 8 MPa. Temperature comparison of the same specimen (number 31).*

6.3 Long term response

The ultimate goal of this thesis was to know the long term response of our composite, once we have analyzed the data and see that is not possible to apply TTS principle to this particular data (which doesn't mean is not applicable to this material), still we have enough curves to extrapolate the results even without applying the principle. Actually, most of the curves analyzed in the previous subchapter demonstrate to tend towards the exponential law we first consider.

Using the Eq.15 and applying it to the experiment with more compliance which should be the worst case for the material as we don't want the material to creep (it is the recovery of experiment 28, specimen 31 at room temperature) we got the parameters D_0= 0.017, D_1=0.004, m=0.33 using minimization of least squares of the error. The compliance calculated with this parameters is measured in [1/GPa] and the time in [seconds].

$$\mathrm{D}(1\ \mathrm{year}) \approx \mathrm{D}_0 + \mathrm{D}_1 \cdot \lambda^{\mathrm{m}} = 0.017 + 0.004 \cdot 31536000^{0.33} = 1.21 \left[\frac{1}{\mathrm{GPa} \cdot \mathrm{Year}}\right] \qquad \text{(Eq.29)}$$

This value means that applying 1 GPa during 1 year the material will deform 121% which is the same as a creep of 0.121 [%/MPa] which is more representative due to the fact that the strength limit for transversal compressive according to the manufacturer is 118 MPa.

Logically if we get the curve from one of the best cases "more solid-like curves" the results are completely different, in the case of Experiment 1 in which we got a very nice curve, the expected value for 1 year is 0.0078 [%/MPa] (the parameters are D_0=1.48, D_1=-1.5, m=-0.0041) which is 15 times less. The difference is bigger the more long we want to extrapolate the results. However, what we can certainly say about the material creep response is that is much less that we first though, and the material behaves very solid-like so the viscoelasticity is almost negligible.

7 Conclusions

Even though the results don't seem to be what we first expected to observe, we got interesting results that actually demonstrates that the viscoelasticity is happening at room temperature and at relatively low stresses, but it is very low compared to the elastic deformation. However we had to face several problems related to the testing machines and specimens that hadn't an immediate solution.

The maximum experimental temperature we got was below 57.5°C which is far from the glass transition temperature and no correlation between temperature and creep was observed. Moreover we haven't found evidences that the age effect is correlated with stiffness in the composite studied. However, the main problem of the whole experimental procedure was the accuracy and the resolution (of 1 µm) of the *Electroforce 3510* and hence the repeatability of the tests. Furthermore, we couldn't get any reliable result from *Electroforce 3200* which is more accurate and it has a resolution up to 1 nm, but it is not designed for high force compression test and it presents vibrations which are not desired at all.

Other parameters are also involved to increase the error of the experiment which we have conclude that are the dilatation of the steel shaft due to minimal temperature changes and the parallelism of the specimens which makes a big difference in the calculation of the modulus.

Finally an estimation of the creep response after one year at room temperature has shown disagreement of a factor of 15 between the most divergent experiments. However the conclusion for all the cases is that the material is in fact viscoelastic because it presents creep and recovery. Despite the fact that the magnitude of its viscoelasticity is low, further tests are needed in order to guarantee the safety of the flywheel constructed at our department. However, we have made the first step towards the characterization and additionally; a powerful computer tool has been created to analyze the data. The next logical step for the characterization of the viscoelasticity would be to build a specific testing machine for compressive tests, and avoid using electromagnetically driven machines which are not suitable for a long term compression.

8 Future work

In this chapter we include some guidelines for the next student carrying on with the time dependant characterization of flywheel's materials. The most important action to make for the next student is to build a proper machine to perform the experiments, as the electromagnetically driven machine is not an option, a good idea would be to design and build a manual driven one, in ***Figure 8—1*** is a sketch of what would be an option for that machine, the best aspect of building this, is the fact that the goal of the machine is to analyze the stress relaxation so it can be used for many hours including at night avoiding the maximum of 1 day test. This is very cost effective and the probably most expensive components would be the load cell and the amplifier which can be reused after the study. If it goes well, several machines can be built to compare the results or just to run multiple tests at the same time. This set up is very good and simple because it doesn't even need a strain gauge to control the displacement as long as the endless screw is not reversible.

The experiments could begin loading the specimen up to a specified value making profit out the load cell and then block the driver for the duration of the experiment.

This is probably a good start to characterize the real response of the material. After getting good and consistent data (repeatability), a linearity check could be done at low stress seeing if the material responds as it is supposed to, in other words, check if the stress relaxation curves change linearly by modifying the stress applied. This is much modest start compared to using TTSP from the very beginning without any idea of the real behavior of the material but it can slowly acquire more consistent data.

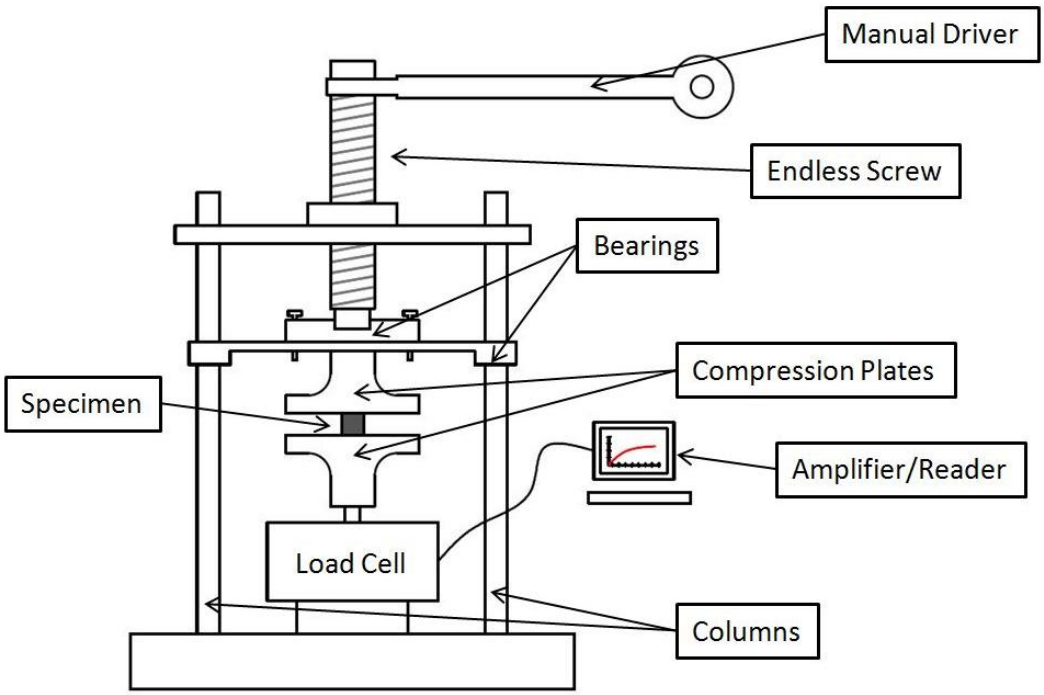

Figure 8—1. Manual *compressive machine for analyzing the stress relaxation.*

The next step could be to make a study of all the directions of the material; to see if both possible orientations for transversal response are the same or it varies (shouldn't be a lot).

Moreover, having 3 or more of these machines, it would be interesting to observe the very long term response of at least one specimen, at least the relaxation after 1 month. This will provide useful data to compare the predictions with the reality.

It would be possible to incorporate a convection oven to elevate the temperature and make the TTSP experiments. But I don't recommend doing so without getting a lot of consistent data before.

Furthermore, all the Scilab tools I have created can be used in that case to analyze the obtained data quickly and get the parameters for the characterization.

Finally, apart from the machine showed in ***Figure 8—1*** it is possible to design a creep machine which is nothing but a dead weight over the specimen and a strain gauge on the lateral surface of the specimen recording the strain change over time. The problem with creep machine is that the specimens are so small that it would be very difficult to incorporate the strain gauges it also would be difficult to read the values of the creep because, as said in the conclusions of the thesis, it is very small. But it is another option that can be implemented indeed.

9 References

[1] A. S. W. a. K.R.Rajagopal, in *Mechanical Response of Polymers an introduction*, Cambridge University Press, 2000.

[2] D. V. a. T.S.Gates, "Compressive Creep of IM7/K3B Composite and the Effects of Physical Aging on Viscoelastic Behavior," Hampton, NASA Langley Research Center, March 1997.

[3] E.J.Barbero, "Time-temperature-age superposition principle for predicting long-term response of linear viscoelastic materials," in *Creep and fatigue in polymer matrix composites*, West Virginia University, Woodhead publishing, 2011.

[4] K. M. P. E. L. G. M. G. Ali Nekouzadeh, "A simplified approach to quasi-linear viscoelastic modeling," St. Louis, Missouri, USA, J Biomech. , 2007.

[5] P. Provenzano, R. K. T. Lakes and R. Vanderby, "Non-linear ligament viscoelasticity," 2001, pp. 908-914.

[6] John Wiley & Sons Inc, in *Fundamental principles of polymeric materials*, 2012, pp. 285-286.

[7] W. G. a. I. E. N.W Tschoegl, "Mechanics of Time-Dependent Materials," Netherlands, Kluwer Academic Publishers, 2002.

[8] R. D. M. a. J. Kubat, "Time and temperature dependent deformation of (PEEK)," in *Mechanics of Composite Materials. Vol 33 No 6.*, 1997.

[9] R.S.Lakes, "Viscoelastic measurement techniques," University of Wisconsin-Madison, published 8 March 2004.

[10] J. K. Robert D. Maksimov, "Time and temperature Dependent deformation of Poly Ether Ether Ketone (PEEK)," Mechanics of Composite Materials, Vol 33, No 6., 1997.

[11] S. C. A. R. G. A. Anne-Gaëlle Denay, "Creep compression behaviour of a polyurethane foam from cryogenic temperatures: size effect and long term prediction," France, EDP Sciences, 2010.

[12] BOSE, "Electroforce@ 3200 Series III Test Instruments Reference Manual".

[13] BOSE, "WinTest® 7 Software Reference Manual".

[14] BOSE, "Electroforce® 3510 Test Instrument Reference Manual".

[15] D. P. John Dealy, "Time-Temperature Superposition - A Users Guide," McGill University and University of Pittsburgh, July 2009.